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THE PHYSICAL REVIEW

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THE

PHYSICAL REVIEW

A QUANTUM THEORY OF THE SCATTERING OF X-RAYS BY LIGHT ELEMENTS

By Arthur H. Compton

Abstract

A quantum theory of the scattering of X-rays and γ-rays by light elements. —The hypothesis is suggested that when an X-ray quantum is scattered it spends all of its energy and momentum upon some particular electron. This electron in turn scatters the ray in some definite direction. The change in momentum of the X-ray quantum due to the change in its direction of propagation results in a recoil of the scattering electron. The energy in the scattered quantum is thus less than the energy in the primary quantum by the kinetic energy of recoil of the scattering electron. The corresponding *increase in the wave-length of the scattered beam* is $\lambda_\theta - \lambda_0 = (2h/mc)\sin^2\frac{1}{2}\theta = 0.0484\sin^2\frac{1}{2}\theta$, where h is the Planck constant, m is the mass of the scattering electron, c is the velocity of light, and θ is the angle between the incident and the scattered ray. Hence the increase is independent of the wave-length. *The distribution of the scattered radiation* is found, by an indirect and not quite rigid method, to be concentrated in the forward direction according to a definite law (Eq. 27). The total energy removed from the primary beam comes out less than that given by the classical Thomson theory in the ratio $1/(1+2\alpha)$, where $\alpha = h/mc\lambda_0 = 0.0242/\lambda_0$. Of this energy a fraction $(1+\alpha)/(1+2\alpha)$ reappears as scattered radiation, while the remainder is truly absorbed and transformed into kinetic energy of recoil of the scattering electrons. Hence, if σ_0 is the *scattering absorption coefficient* according to the classical theory, the coefficient according to this theory is $\sigma = \sigma_0/(1+2\alpha) = \sigma_s + \sigma_a$, where σ_s is the true scattering coefficient $[(1+\alpha)\sigma/(1+2\alpha)^2]$, and σ_a is the coefficient of absorption due to scattering $[\alpha\sigma/(1+2\alpha)^2]$. Unpublished experimental results are given which show that for graphite and the Mo–K radiation the scattered radiation is longer than the primary, the observed difference $(\lambda_{\pi/2} - \lambda_0 = .022)$ being close to the computed value .024. In the case of scattered γ-rays, the wave-length has been found to vary with θ in agreement with the theory, increasing from .022 A (primary) to .068 A ($\theta = 135°$). Also the velocity of secondary β-rays excited in light elements by γ-rays agrees with the suggestion that they are recoil electrons. As for the predicted variation of absorption with λ, Hewlett's results for carbon for wave-lengths below 0.5 A are in excellent agreement with this theory; also the predicted concentration in the forward direction is shown to be in agreement with the experimental results,

both for X-rays and γ-rays. This remarkable *agreement between experiment and theory* indicates clearly that scattering is a quantum phenomenon and can be explained without introducing any new hypothesis as to the size of the electron or any new constants; also that a radiation quantum carries with it momentum as well as energy. The restriction to light elements is due to the assumption that the constraining forces acting on the scattering electrons are negligible, which is probably legitimate only for the lighter elements.

Spectrum of K-rays from Mo scattered by graphite, as compared with the spectrum of the primary rays, is given in Fig. 4, showing the change of wave-length.

Radiation from a moving isotropic radiator.—It is found that in a direction θ with the velocity, $I_\theta/I' = (1-\beta)^2/(1-\beta\cos\theta)^4 = (\nu_\theta/\nu')^4$. For the total radiation from a black body in motion to an observer at rest, $I/I' = (T/T')^4 = (\nu_m/\nu_m')^4$, where the primed quantities refer to the body at rest.

J. J. Thomson's classical theory of the scattering of X-rays, though supported by the early experiments of Barkla and others, has been found incapable of explaining many of the more recent experiments. This theory, based upon the usual electrodynamics, leads to the result that the energy scattered by an electron traversed by an X-ray beam of unit intensity is the same whatever may be the wave-length of the incident rays. Moreover, when the X-rays traverse a thin layer of matter, the intensity of the scattered radiation on the two sides of the layer should be the same. Experiments on the scattering of X-rays by light elements have shown that these predictions are correct when X-rays of moderate hardness are employed; but when very hard X-rays or γ-rays are employed, the scattered energy is found to be decidedly less than Thomson's theoretical value, and to be strongly concentrated on the emergent side of the scattering plate.

Several years ago the writer suggested that this reduced scattering of the very short wave-length X-rays might be the result of interference between the rays scattered by different parts of the electron, if the electron's diameter is comparable with the wave-length of the radiation. By assuming the proper radius for the electron, this hypothesis supplied a quantitative explanation of the scattering for any particular wave-length. But recent experiments have shown that the size of the electron which must thus be assumed increases with the wave-length of the X-rays employed,[1] and the conception of an electron whose size varies with the wave-length of the incident rays is difficult to defend.

Recently an even more serious difficulty with the classical theory of X-ray scattering has appeared. It has long been known that secondary γ-rays are softer than the primary rays which excite them, and recent experiments have shown that this is also true of X-rays. By a spectroscopic examination of the secondary X-rays from graphite, I have, indeed,

[1] A. H. Compton, Bull. Nat. Research Council, No. 20, p. 10 (Oct., 1922).

been able to show that only a small part, if any, of the secondary X-radiation is of the same wave-length as the primary.[1] While the energy of the secondary X-radiation is so nearly equal to that calculated from Thomson's classical theory that it is difficult to attribute it to anything other than true scattering,[2] these results show that if there is any scattering comparable in magnitude with that predicted by Thomson, it is of a greater wave-length than the primary X-rays.

Such a change in wave-length is directly counter to Thomson's theory of scattering, for this demands that the scattering electrons, radiating as they do because of their forced vibrations when traversed by a primary X-ray, shall give rise to radiation of exactly the same frequency as that of the radiation falling upon them. Nor does any modification of the theory such as the hypothesis of a large electron suggest a way out of the difficulty. This failure makes it appear improbable that a satisfactory explanation of the scattering of X-rays can be reached on the basis of the classical electrodynamics.

The Quantum Hypothesis of Scattering

According to the classical theory, each X-ray affects every electron in the matter traversed, and the scattering observed is that due to the combined effects of all the electrons. From the point of view of the quantum theory, we may suppose that any particular quantum of X-rays is not scattered by all the electrons in the radiator, but spends all of its energy upon some particular electron. This electron will in turn scatter the ray in some definite direction, at an angle with the incident beam. This bending of the path of the quantum of radiation results in a change in its momentum. As a consequence, the scattering electron will recoil with a momentum equal to the change in momentum of the X-ray. The energy in the scattered ray will be equal to that in the incident ray minus the kinetic energy of the recoil of the scattering electron; and since the scattered ray must be a complete quantum, the frequency will be reduced in the same ratio as is the energy. Thus on the quantum theory we should expect the wave-length of the scattered X-rays to be greater than that of the incident rays.

The effect of the momentum of the X-ray quantum is to set the

[1] In previous papers (Phil. Mag. **41**, 749, 1921; Phys. Rev. **18**, 96, 1921) I have defended the view that the softening of the secondary X-radiation was due to a considerable admixture of a form of fluorescent radiation. Gray (Phil. Mag. **26**, 611, 1913; Frank. Inst. Journ., Nov., 1920, p. 643) and Florance (Phil. Mag. **27**, 225, 1914) have considered that the evidence favored true scattering, and that the softening is in some way an accompaniment of the scattering process. The considerations brought forward in the present paper indicate that the latter view is the correct one.

[2] A. H. Compton, loc. cit., p. 16.

scattering electron in motion at an angle of less than 90° with the primary beam. But it is well known that the energy radiated by a moving body is greater in the direction of its motion. We should therefore expect, as is experimentally observed, that the intensity of the scattered radiation should be greater in the general direction of the primary X-rays than in the reverse direction.

The change in wave-length due to scattering.—Imagine, as in Fig. 1*A*,

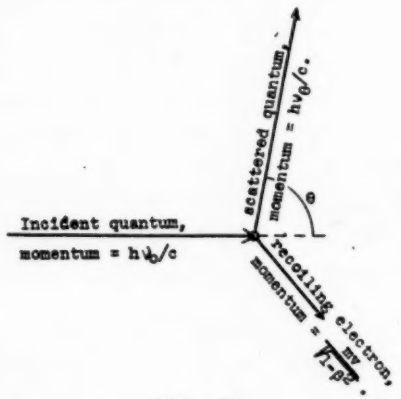

Fig. 1 A

Fig. 1 B

that an X-ray quantum of frequency ν_0 is scattered by an electron of mass m. The momentum of the incident ray will be $h\nu_0/c$, where c is the velocity of light and h is Planck's constant, and that of the scattered ray is $h\nu_\theta/c$ at an angle θ with the initial momentum. The principle of the conservation of momentum accordingly demands that the momentum of recoil of the scattering electron shall equal the vector difference between the momenta of these two rays, as in Fig. 1*B*. The momentum of the electron, $m\beta c/\sqrt{1-\beta^2}$, is thus given by the relation

$$\left(\frac{m\beta c}{\sqrt{1-\beta^2}}\right)^2 = \left(\frac{h\nu_0}{c}\right)^2 + \left(\frac{h\nu_\theta}{c}\right)^2 + 2\frac{h\nu_0}{c}\cdot\frac{h\nu_\theta}{c}\cos\theta, \qquad (1)$$

where β is the ratio of the velocity of recoil of the electron to the velocity of light. But the energy $h\nu_\theta$ in the scattered quantum is equal to that of the incident quantum $h\nu_0$ less the kinetic energy of recoil of the scattering electron, *i.e.*,

$$h\nu_\theta = h\nu_0 - mc^2\left(\frac{1}{\sqrt{1-\beta^2}} - 1\right). \qquad (2)$$

We thus have two independent equations containing the two unknown quantities β and ν_θ. On solving the equations we find

$$\nu_\theta = \nu_0/(1 + 2\alpha\sin^2\tfrac{1}{2}\theta), \qquad (3)$$

where

$$\alpha = h\nu_0/mc^2 = h/mc\lambda_0. \tag{4}$$

Or in terms of wave-length instead of frequency,

$$\lambda_\theta = \lambda_0 + (2h/mc)\sin^2\tfrac{1}{2}\theta. \tag{5}$$

It follows from Eq. (2) that $1/(1-\beta^2) = \{1+\alpha[1-(\nu_\theta/\nu_0)]\}^2$, or solving explicitly for β

$$\beta = 2\alpha\sin\tfrac{1}{2}\theta\,\frac{\sqrt{1+(2\alpha+\alpha^2)\sin^2\tfrac{1}{2}\theta}}{1+2(\alpha+\alpha^2)\sin^2\tfrac{1}{2}\theta}. \tag{6}$$

Eq. (5) indicates an increase in wave-length due to the scattering process which varies from a few per cent in the case of ordinary X-rays to more than 200 per cent in the case of γ-rays scattered backward. At the same time the velocity of the recoil of the scattering electron, as calculated from Eq. (6), varies from zero when the ray is scattered directly forward to about 80 per cent of the speed of light when a γ-ray is scattered at a large angle.

It is of interest to notice that according to the classical theory, if an X-ray were scattered by an electron moving in the direction of propagation at a velocity $\beta' c$, the frequency of the ray scattered at an angle θ is given by the Doppler principle as

$$\nu_\theta = \nu_0\Big/\left(1+\frac{2\beta'}{1-\beta'}\sin^2\tfrac{1}{2}\theta\right). \tag{7}$$

It will be seen that this is of exactly the same form as Eq. (3), derived on the hypothesis of the recoil of the scattering electron. Indeed, if $\alpha = \beta'/(1-\beta')$ or $\beta' = \alpha/(1+\alpha)$, the two expressions become identical. It is clear, therefore, that so far as the effect on the wave-length is concerned, we may replace the recoiling electron by a scattering electron moving in the direction of the incident beam at a velocity such that

$$\bar{\beta} = \alpha/(1+\alpha). \tag{8}$$

We shall call $\bar{\beta}c$ the "effective velocity" of the scattering electrons.

Energy distribution from a moving, isotropic radiator.—In preparation for the investigation of the spatial distribution of the energy scattered by a recoiling electron, let us study the energy radiated from a moving, isotropic body. If an observer moving with the radiating body draws a sphere about it, the condition of isotropy means that the probability is equal for all directions of emission of each energy quantum. That is, the probability that a quantum will traverse the sphere between the angles θ' and $\theta' + d\theta'$ with the direction of motion is $\frac{1}{2}\sin\theta' d\theta'$. But

the surface which the moving observer considers a sphere (Fig. 2*A*) is

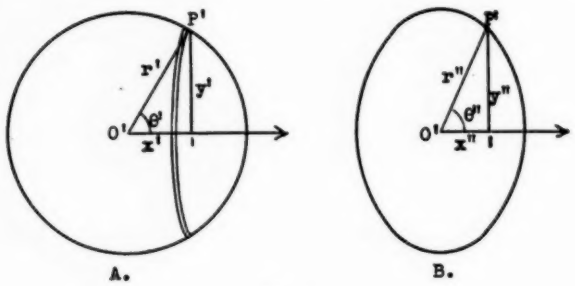

Fig. 2

considered by the stationary observer to be an oblate spheroid whose polar axis is reduced by the factor $\sqrt{1-\beta^2}$. Consequently a quantum of radiation which traverses the sphere at the angle θ', whose tangent is y'/x' (Fig. 2*A*), appears to the stationary observer to traverse the spheroid at an angle θ'' whose tangent is y''/x'' (Fig. 2*B*). Since $x' = x''/\sqrt{1-\beta^2}$ and $y' = y''$, we have

$$\tan\theta' = y'/x' = \sqrt{1-\beta^2}\, y''/x'' = \sqrt{1-\beta^2}\tan\theta'', \tag{9}$$

and

$$\sin\theta' = \frac{\sqrt{1-\beta^2}\tan\theta''}{\sqrt{1+(1-\beta^2)\tan^2\theta''}}. \tag{10}$$

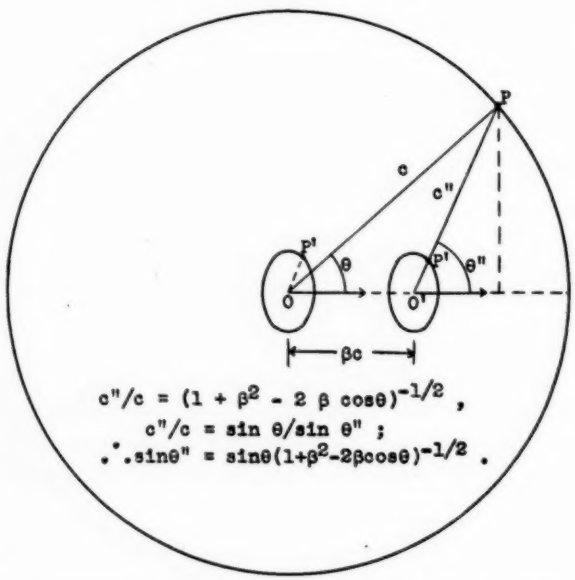

Fig. 3. The ray traversing the moving spheroid at P' at an angle θ'' reaches the stationary spherical surface drawn about O, at the point P, at an angle θ.

Imagine, as in Fig. 3, that a quantum is emitted at the instant $t = 0$, when the radiating body is at O. If it traverses the moving observer's sphere at an angle θ', it traverses the corresponding oblate spheroid, imagined by the stationary observer to be moving with the body, at an angle θ''. After 1 second, the quantum will have reached some point P on a sphere of radius c drawn about O, while the radiator will have moved a distance βc. The stationary observer at P therefore finds that the radiation is coming to him from the point O, at an angle θ with the direction of motion. That is, if the moving observer considers the quantum to be emitted at an angle θ' with the direction of motion, to the stationary observer the angle appears to be θ, where

$$\sin \theta / \sqrt{1 + \beta^2 - 2\beta \cos \theta} = \sin \theta'', \tag{11}$$

and θ'' is given in terms of θ' by Eq. (10). It follows that

$$\sin \theta' = \sin \theta \frac{\sqrt{1 - \beta^2}}{1 - \beta \cos \theta}. \tag{12}$$

On differentiating Eq. (12) we obtain

$$d\theta' = \frac{\sqrt{1 - \beta^2}}{1 - \beta \cos \theta} d\theta. \tag{13}$$

The probability that a given quantum will appear to the stationary observer to be emitted between the angles θ and $\theta + d\theta$ is therefore

$$P_\theta d\theta = P_{\theta'} d\theta' = \tfrac{1}{2} \sin \theta' d\theta',$$

where the values of $\sin \theta'$ and $d\theta'$ are given by Eqs. (12) and (13). Substituting these values we find

$$P_\theta d\theta = \frac{1 - \beta^2}{(1 - \beta \cos \theta)^2} \cdot \tfrac{1}{2} \sin \theta d\theta. \tag{14}$$

Suppose the moving observer notices that n' quanta are emitted per second. The stationary observer will estimate the rate of emission as

$$n'' = n' \sqrt{1 - \beta^2},$$

quanta per second, because of the difference in rate of the moving and stationary clocks. Of these n'' quanta, the number which are emitted between angles θ and $\theta + d\theta$ is $dn'' = n'' \cdot P_\theta d\theta$. But if dn'' per second are emitted at the angle θ, the number per second received by a stationary observer at this angle is $dn = dn''/(1 - \beta \cos \theta)$, since the radiator is approaching the observer at a velocity $\beta \cos \theta$. The energy of each quantum is, however, $h\nu_\theta$, where ν_θ is the frequency of the radiation as

received by the stationary observer.[1] Thus the intensity, or the energy per unit area per unit time, of the radiation received at an angle θ and a distance R is

$$I_\theta = \frac{h\nu_\theta \cdot dn}{2\pi R^2 \sin\theta d\theta} = \frac{h\nu_\theta}{2\pi R^2 \sin\theta d\theta} \frac{n'(1-\beta^2)^{3/2}}{(1-\beta\cos\theta)^3} \tfrac{1}{2} \sin\theta d\theta$$
$$= \frac{n' h\nu_\theta}{4\pi R^2} \frac{(1-\beta^2)^{3/2}}{(1-\beta\cos\theta)^3}. \tag{15}$$

If the frequency of the oscillator emitting the radiation is measured by an observer moving with the radiator as ν', the stationary observer judges its frequency to be $\nu'' = \nu'\sqrt{1-\beta^2}$, and, in virtue of the Doppler effect, the frequency of the radiation received at an angle θ is

$$\nu_\theta = \nu''/(1-\beta\cos\theta) = \nu'[\sqrt{1-\beta^2}/(1-\beta\cos\theta)]. \tag{16}$$

Substituting this value of ν_θ in Eq. (15) we find

$$I_\theta = \frac{n' h\nu'}{4\pi R^2} \frac{(1-\beta^2)^2}{(1-\beta\cos\theta)^4}. \tag{17}$$

But the intensity of the radiation observed by the moving observer at a distance R from the source is $I' = n' h\nu'/4\pi R^2$. Thus,

$$I_\theta = I'[(1-\beta)^2/(1-\beta\cos\theta)^4] \tag{18}$$

is the intensity of the radiation received at an angle θ with the direction of motion of an isotropic radiator, which moves with a velocity βc, and which would radiate with intensity I' if it were at rest.[2]

It is interesting to note, on comparing Eqs. (16) and (18), that

$$I_\theta/I' = (\nu_\theta/\nu')^4. \tag{19}$$

[1] At first sight the assumption that the quantum which to the moving observer had energy $h\nu'$ will be $h\nu$ for the stationary observer seems inconsistent with the energy principle. When one considers, however, the work done by the moving body against the back-pressure of the radiation, it is found that the energy principle is satisfied. The conclusion reached by the present method of calculation is in exact accord with that which would be obtained according to Lorenz's equations, by considering the radiation to consist of electromagnetic waves.

[2] G. H. Livens gives for I_θ/I' the value $(1-\beta\cos\theta)^{-2}$ ("The Theory of Electricity," p. 600, 1918). At small velocities this value differs from the one here obtained by the factor $(1-\beta\cos\theta)^{-2}$. The difference is due to Livens' neglect of the concentration of the radiation in the small angles, as expressed by our Eq. (14). Cunningham ("The Principle of Relativity," p. 60, 1914) shows that if a plane wave is emitted by a radiator moving in the direction of propagation with a velocity βc, the intensity I received by a stationary observer is greater than the intensity I' estimated by the moving observer, in the ratio $(1-\beta^2)/(1-\beta)^2$, which is in accord with the value calculated according to the methods here employed.

The change in frequency given in Eq. (16) is that of the usual relativity theory. I have not noticed the publication of any result which is the equivalent of my formula (18) for the intensity of the radiation from a moving body.

This result may be obtained very simply for the total radiation from a black body, which is a special case of an isotropic radiator. For, suppose such a radiator is moving so that the frequency of maximum intensity which to a moving observer is ν_m' appears to the stationary observer to be ν_m. Then according to Wien's law, the apparent temperature T, as estimated by the stationary observer, is greater than the temperature T' for the moving observer by the ratio $T/T' = \nu_m/\nu_m'$. According to Stefan's law, however, the intensity of the total radiation from a black body is proportional to T^4; hence, if I and I' are the intensities of the radiation as measured by the stationary and the moving observers respectively,

$$I/I' = (T/T')^4 = (\nu_m/\nu_m')^4. \tag{20}$$

The agreement of this result with Eq. (19) may be taken as confirming the correctness of the latter expression.

The intensity of scattering from recoiling electrons.—We have seen that the change in frequency of the radiation scattered by the recoiling electrons is the same as if the radiation were scattered by electrons moving in the direction of propagation with an effective velocity $\bar{\beta} = \alpha/(1 + \alpha)$, where $\alpha = h/mc\lambda_0$. It seems obvious that since these two methods of calculation result in the same change in wave-length, they must also result in the same change in intensity of the scattered beam. This assumption is supported by the fact that we find, as in Eq. 19, that the change in intensity is in certain special cases a function only of the change in frequency. I have not, however, succeeded in showing rigidly that if two methods of scattering result in the same relative wave-lengths at different angles, they will also result in the same relative intensity at different angles. Nevertheless, we shall assume that this proposition is true, and shall proceed to calculate the relative intensity of the scattered beam at different angles on the hypothesis that the scattering electrons are moving in the direction of the primary beam with a velocity $\bar{\beta} = \alpha/(1 + \alpha)$. If our assumption is correct, the results of the calculation will apply also to the scattering by recoiling electrons.

To an observer moving with the scattering electron, the intensity of the scattering at an angle θ', according to the usual electrodynamics, should be proportional to $(1 + \cos^2\theta')$, if the primary beam is unpolarized. On the quantum theory, this means that the probability that a quantum will be emitted between the angles θ' and $\theta' + d\theta'$ is proportional to $(1 + \cos^2\theta')\cdot\sin\theta' d\theta'$, since $2\pi \sin\theta' d\theta'$ is the solid angle included between θ' and $\theta' + d\theta'$. This may be written $P_{\theta'}d\theta' = k(1 + \cos^2\theta')\sin\theta' d\theta'$.

The factor of proportionality k may be determined by performing the integration

$$\int_0^\pi P_{\theta'}d\theta' = k\int_0^\pi (1 + \cos^2\theta')\sin\theta' d\theta' = 1,$$

with the result that $k = 3/8$. Thus

$$P_{\theta'}d\theta' = (3/8)(1 + \cos^2\theta')\sin\theta' d\theta' \qquad (21)$$

is the probability that a quantum will be emitted at the angle θ' as measured by an observer moving with the scattering electron.

To the stationary observer, however, the quantum ejected at an angle θ' appears to move at an angle θ with the direction of the primary beam, where $\sin\theta'$ and $d\theta'$ are as given in Eqs. (12) and (13). Substituting these values in Eq. (21), we find for the probability that a given quantum will be scattered between the angles θ and $\theta + d\theta$,

$$P_\theta d\theta = \tfrac{3}{8}\sin\theta d\theta \frac{(1-\beta^2)\{(1+\beta^2)(1+\cos^2\theta) - 4\beta\cos\theta\}}{(1-\beta\cos\theta)^4}. \qquad (22)$$

Suppose the stationary observer notices that n quanta are scattered per second. In the case of the radiator emitting n'' quanta per second while approaching the observer, the n''th quantum was emitted when the radiator was nearer the observer, so that the interval between the receipt of the 1st and the n''th quantum was less than a second. That is, more quanta were received per second than were emitted in the same time. In the case of scattering, however, though we suppose that each scattering electron is moving forward, the nth quantum is scattered by an electron starting from the same position as the 1st quantum. Thus the number of quanta received per second is also n.

We have seen (Eq. 3) that the frequency of the quantum received at an angle θ is $\nu_\theta = \nu_0/(1 + 2\alpha\sin^2\tfrac{1}{2}\theta) = \nu_0/\{1 + \alpha(1 - \cos\theta)\}$, where ν_0, the frequency of the incident beam, is also the frequency of the ray scattered in the direction of the incident beam. The energy scattered per second at the angle θ is thus $nh\nu_\theta P_\theta d\theta$, and the intensity, or energy per second per unit area, of the ray scattered to a distance R is

$$I_\theta = \frac{nh\nu_\theta P_\theta d\theta}{2\pi R^2\sin\theta d\theta}$$

$$= \frac{nh}{2\pi R^2}\cdot\frac{\nu_0}{1+\alpha(1-\cos\theta)}\cdot\frac{3}{8}\cdot\frac{(1-\beta^2)\{(1+\beta^2)(1+\cos^2\theta)-4\beta\cos\theta\}}{(1-\beta\cos\theta)^4}.$$

Substituting for β its value $\alpha/(1 + \alpha)$, and reducing, this becomes

$$I = \frac{3nh\nu_0}{16\pi R}\frac{(1+2\alpha)\{1+\cos^2\theta+2\alpha(1+\alpha)(1-\cos\theta)^2\}}{(1+\alpha-\alpha\cos\theta)^5}. \qquad (23)$$

In the forward direction, where $\theta = 0$, the intensity of the scattered beam is thus

$$I_0 = \frac{3}{8\pi}\frac{nh\nu_0}{R^2}(1 + 2\alpha). \tag{24}$$

Hence

$$\frac{I_\theta}{I_0} = \frac{1}{2}\frac{1 + \cos^2\theta + 2\alpha(1 + \alpha)(1 - \cos\theta)^2}{\{1 + \alpha(1 - \cos\theta)\}^5}. \tag{25}$$

On the hypothesis of recoiling electrons, however, for a ray scattered directly forward, the velocity of recoil is zero (Eq. 6). Since in this case the scattering electron is at rest, the intensity of the scattered beam should be that calculated on the basis of the classical theory, namely,

$$I_0 = I(Ne^4/R^2m^2c^4), \tag{26}$$

where I is the intensity of the primary beam traversing the N electrons which are effective in scattering. On combining this result with Eq. (25), we find for the intensity of the X-rays scattered at an angle θ with the incident beam,

$$I = I\frac{Ne^4}{2R^2m^2c^4}\frac{1 + \cos^2\theta + 2\alpha(1 + \alpha)(1 - \cos\theta)^2}{\{1 + \alpha(1 - \cos\theta)\}^5}. \tag{27}$$

The calculation of the energy removed from the primary beam may now be made without difficulty. We have supposed that n quanta are scattered per second. But on comparing Eqs. (24) and (26), we find that

$$n = \frac{8\pi}{3}\frac{INe^4}{h\nu_0m^2c^4(1 + 2\alpha)}.$$

The energy removed from the primary beam per second is $nh\nu_0$. If we define *the scattering absorption coefficient* as the fraction of the energy of the primary beam removed by the scattering process per unit length of path through the medium, it has the value

$$\sigma = \frac{nh\nu_0}{I} = \frac{8\pi}{3}\frac{Ne^4}{m^2c^4}\cdot\frac{1}{1 + 2\alpha} = \frac{\sigma_0}{1 + 2\alpha}, \tag{28}$$

where N is the number of scattering electrons per unit volume, and σ_0 is the scattering coefficient calculated on the basis of the classical theory.[1]

In order to determine the total energy truly scattered, we must integrate the scattered intensity over the surface of a sphere surrounding the scattering material, *i.e.*, $\epsilon_s = \int_0^\pi I_\theta \cdot 2\pi R^2 \sin\theta d\theta$. On substituting the value of I_θ from Eq. (27), and integrating, this becomes

$$\epsilon_s = \frac{8\pi}{3}\frac{INe^4}{m^2c^4}\frac{1 + \alpha}{(1 + 2\alpha)^2}.$$

[1] Cf. J. J. Thomson, "Conduction of Electricity through Gases," 2d ed., p. 325.

The *true scattering coefficient* is thus

$$\sigma_s = \frac{8\pi}{3}\frac{Ne^4}{m^2c^4}\frac{1+\alpha}{(1+2\alpha)^2} = \sigma_0\frac{1+\alpha}{(1+2\alpha)^2}. \qquad (29)$$

It is clear that the difference between the total energy removed from the primary beam and that which reappears as scattered radiation is the energy of recoil of the scattering electrons. This difference represents, therefore, a type of true absorption resulting from the scattering process. The corresponding *coefficient of true absorption due to scattering* is

$$\sigma_a = \sigma - \sigma_s = \frac{8\pi}{3}\frac{Ne^4}{m^2c^4}\frac{\alpha}{(1+2\alpha)^2} = \sigma_0\frac{\alpha}{(1+2\alpha)^2}. \qquad (30)$$

Experimental Test.

Let us now investigate the agreement of these various formulas with exper ments on the change of wave-length due to scattering, and on the magnitude of the scattering of X-rays and γ-rays by light elements.

Wave-length of the scattered rays.—If in Eq. (5) we substitute the accepted values of h, m, and c, we obtain

$$\lambda_\theta = \lambda_0 + 0.0484 \sin^2 \tfrac{1}{2}\theta, \qquad (31)$$

if λ is expressed in Angström units. It is perhaps surprising that the increase should be the same for all wave-lengths. Yet, as a result of an extensive experimental study of the change in wave-length on scattering, the writer has concluded that "over the range of primary rays from 0.7 to 0.025 A, the wave-length of the secondary X-rays at 90° with the incident beam is roughly 0.03 A greater than that of the primary beam which excites it." [1] Thus the experiments support the theory in showing a wave-length increase which seems independent of the incident wave-length, and which also is of the proper order of magnitude.

A quantitative test of the accuracy of Eq. (31) is possible in the case of the characteristic K-rays from molybdenum when scattered by graphite. In Fig. 4 is shown a spectrum of the X-rays scattered by graphite at right angles with the primary beam, when the graphite is traversed by X-rays from a molybdenum target.[2] The solid line represents the spectrum of these scattered rays, and is to be compared with the broken line, which represents the spectrum of the primary rays, using the same slits and crystal, and the same potential on the tube. The primary spectrum is, of course, plotted on a much smaller scale than

[1] A. H. Compton, Bull. N. R. C., No. 20, p. 17 (1922).

[2] It is hoped to publish soon a description of the experiments on which this figure is based.

the secondary. The zero point for the spectrum of both the primary and secondary X-rays was determined by finding the position of the first order lines on both sides of the zero point.

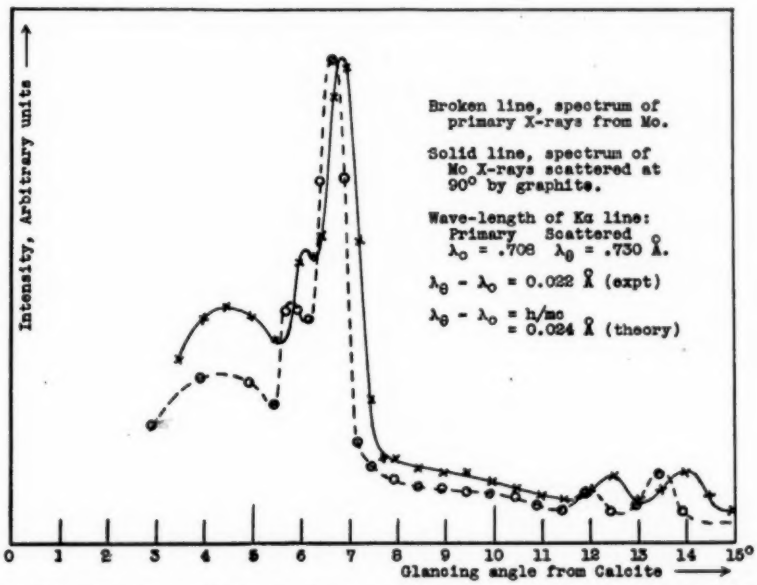
Intensity, Arbitrary units
Broken line, spectrum of primary X-rays from Mo.
Solid line, spectrum of Mo X-rays scattered at 90° by graphite.
Wave-length of Kα line:
Primary Scattered
λ0 = .708 λθ = .730 Å.
λθ - λ0 = 0.022 Å (expt)
λθ - λ0 = h/mc = 0.024 Å (theory)
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15°
Glancing angle from Calcite

Fig. 4. Spectrum of molybdenum X-rays scattered by graphite, compared with the spectrum of the primary X-rays, showing an increase in wave-length on scattering.

It will be seen that the wave-length of the scattered rays is unquestionably greater than that of the primary rays which excite them. Thus the Kα line from molybdenum has a wave-length 0.708 A. The wave-length of this line in the scattered beam is found in these experiments, however, to be 0.730 A. That is,

$$\lambda_\theta - \lambda_0 = 0.022 \text{ A} \quad \text{(experiment)}.$$

But according to the present theory (Eq. 5),

$$\lambda_\theta - \lambda_0 = 0.0484 \sin^2 45° = 0.024 \text{ A} \quad \text{(theory)},$$

which is a very satisfactory agreement.

The variation in wave-length of the scattered beam with the angle is illustrated in the case of γ-rays. The writer has measured [1] the mass absorption coefficient in lead of the rays scattered at different angles when various substances are traversed by the hard γ-rays from RaC. The mean results for iron, aluminium and paraffin are given in column 2 of Table I. This variation in absorption coefficient corresponds to a

[1] A. H. Compton, Phil. Mag. **41**, 760 (1921).

difference in wave-length at the different angles. Using the value given by Hull and Rice for the mass absorption coefficient in lead for wave-length 0.122, 3.0, remembering[1] that the characteristic fluorescent absorption τ/ρ is proportional to λ^3, and estimating the part of the absorption due to scattering by the method described below, I find for the wave-lengths corresponding to these absorption coefficients the values given in the fourth column of Table I. That this extrapolation is very

TABLE I

Wave-length of Primary and Scattered γ-rays

	Angle	μ/ρ	τ/ρ	λ obs.	λ calc.
Primary	0°	.076	.017	0.022 A	(0.022 A)
Scattered	45°	.10	.042	.030	0.029
"	90°	.21	.123	.043	0.047
"	135°	.59	.502	.068	0.063

nearly correct is indicated by the fact that it gives for the primary beam a wave-length 0.022 A. This is in good accord with the writer's value 0.025 A, calculated from the scattering of γ-rays by lead at small angles,[2] and with Ellis' measurements from his β-ray spectra, showing lines of wave-length .045, .025, .021 and .020 A, with line .020 the strongest.[3] Taking $\lambda_0 = 0.022$ A, the wave-lengths at the other angles may be calculated from Eq. (31). The results, given in the last column of Table I., and shown graphically in Fig. 5, are in satisfactory accord with the measured values. There is thus good reason for believing that Eq. (5) represents accurately the wave-length of the X-rays and γ-rays scattered by light elements.

Velocity of recoil of the scattering electrons.—The electrons which recoil in the process of the scattering of ordinary X-rays have not been observed. This is probably because their number and velocity is usually small compared with the number and velocity of the photoelectrons ejected as a result of the characteristic fluorescent absorption. I have pointed out elsewhere,[4] however, that there is good reason for believing that most of the secondary β-rays excited in light elements by the action of γ-rays are such recoil electrons. According to Eq. (6), the velocity of these electrons should vary from 0, when the γ-ray is scattered forward, to $v_{max} = \beta_{max}c = 2c\alpha[(1 + \alpha)/(1 + 2\alpha + 2\alpha^2)]$, when the γ-ray quantum

[1] Cf. L. de Broglie, Jour. de Phys. et Rad. **3**, 33 (1922); A. H. Compton, Bull. N. R. C., No. 20, p. 43 (1922).

[2] A. H. Compton, Phil. Mag. **41**, 777 (1921).

[3] C. D. Ellis, Proc. Roy. Soc. A, **101**, 6 (1922).

[4] A. H. Compton, Bull. N. R. C., No. 20, p. 27 (1922).

is scattered backward. If for the hard γ-rays from radium C, $\alpha = 1.09$, corresponding to $\lambda = 0.022$ A, we thus obtain $\beta_{max} = 0.82$. The effective velocity of the scattering electrons is, therefore (Eq. 8), $\bar{\beta} = 0.52$. These results are in accord with the fact that the average velocity of the

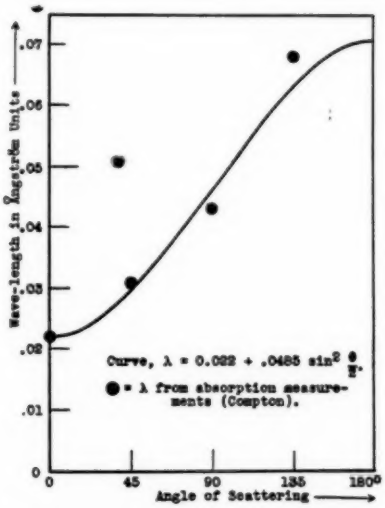

Fig. 5. The wave-length of scattered γ-rays at different angles with the primary beam, showing an increase at large angles similar to a Doppler effect.

β-rays excited by the γ-rays from radium is somewhat greater than half that of light.[1]

Absorption of X-rays due to scattering.—Valuable information concerning the magnitude of the scattering is given by the measurements of the absorption of X-rays due to scattering. Over a wide range of wave-lengths, the formula for the total mass absorption, $\mu/\rho = \kappa\lambda^3 + \sigma/\rho$, is found to hold, where μ is the linear absorption coefficient, ρ is the density, κ is a constant, and σ is the energy loss due to the scattering process. Usually the term $\kappa\lambda^3$, which represents the fluorescent absorption, is the more important; but when light elements and short wave-lengths are employed, the scattering process accounts for nearly all the energy loss. In this case, the constant κ can be determined by measurements on the longer wave-lengths, and the value of σ/ρ can then be estimated with considerable accuracy for the shorter wave-lengths from the observed values of μ/ρ.

Hewlett has measured the total absorption coefficient for carbon over a wide range of wave-lengths.[2] From his data for the longer wave-

[1] E. Rutherford, Radioactive Substances and their Radiations, p. 273.

[2] C. W. Hewlett, Phys. Rev. **17**, 284 (1921).

lengths I estimate the value of κ to be 0.912, if λ is expressed in A. On subtracting the corresponding values of $\kappa\lambda^3$ from his observed values of μ/ρ, the values of σ/ρ represented by the crosses of Fig. 6 are obtained.

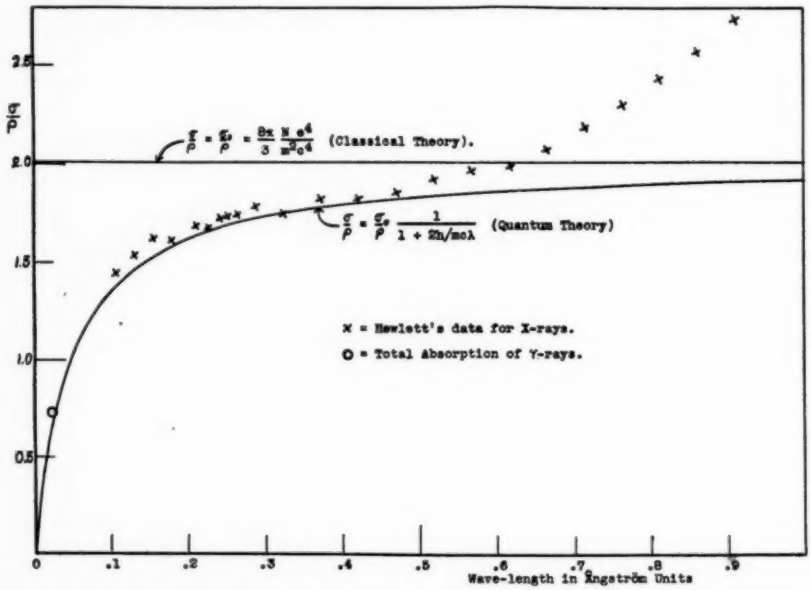

Fig. 6. The absorption in carbon due to scattering, for homogeneous X-rays.

The value of σ_0/ρ as calculated for carbon from Thomson's formula is shown by the horizontal line at $\sigma/\rho = 0.201$. The values of σ/ρ calculated from Eq. (28) are represented by the solid curve. The circle shows the experimental value of the total absorption of γ-rays by carbon, which on the present view is due wholly to the scattering process.

For wave-lengths less than 0.5 A, where the test is most significant, the agreement is perhaps within the experimental error. Experiments by Owen,[1] Crowther,[2] and Barkla and Ayers[3] show that at about 0.5 A the "excess scattering" begins to be appreciable, increasing rapidly in importance at the longer wave-lengths.[4] It is probably this effect which results in the increase of the scattering absorption above the theoretical value for the longer wave-lengths. Thus the experimental values of the absorption due to scattering seem to be in satisfactory accord with the present theory.

True absorption due to scattering has not been noticed in the case of

[1] E. A. Owen, Proc. Camb. Phil. Soc. **16**, 165 (1911).
[2] J. A. Crowther, Proc. Roy. Soc. **86**, 478 (1912).
[3] Barkla and Ayers, Phil. Mag. **21**, 275 (1911).
[4] Cf. A. H. Compton, Washington University Studies, **8**, 109 ff. (1921).

X-rays. In the case of hard γ-rays, however, Ishino has shown [1] that there is true absorption as well as scattering, and that for the lighter elements the true absorption is proportional to the atomic number. That is, this absorption is proportional to the number of electrons present, just as is the scattering. He gives for the true mass absorption coefficient of the hard γ-rays from RaC in both aluminium and iron the value 0.021. According to Eq. (30), the true mass absorption by aluminium should be 0.021 and by iron, 0.020, taking the effective wave-length of the rays to be 0.022 A. The difference between the theory and the experiments is less than the probable experimental error.

Ishino has also estimated the true mass scattering coefficients of the hard γ-rays from RaC by aluminium and iron to be 0.045 and 0.042 respectively.[2] These values are very far from the values 0.193 and 0.187 predicted by the classical theory. But taking $\lambda = 0.022$ A, as before, the corresponding values calculated from Eq. (29) are 0.040 and 0.038, which do not differ seriously from the experimental values.

It is well known that for soft X-rays scattered by light elements the total scattering is in accord with Thomson's formula. This is in agreement with the present theory, according to which the true scattering coefficient σ_s approaches Thomson's value σ_0 when $\alpha \equiv h/mc\lambda$ becomes small (Eq. 29).

The relative intensity of the X-rays scattered in different directions with the primary beam.—Our Eq. (27) predicts a concentration of the energy in the forward direction. A large number of experiments on the scattering of X-rays have shown that, except for the excess scattering at small angles, the ionization due to the scattered beam is symmetrical on the emergence and incidence sides of a scattering plate. The difference in intensity on the two sides according to Eq. (27) should, however, be noticeable. Thus if the wave-length is 0.7 A, which is probably about that used by Barkla and Ayers in their experiments on the scattering by carbon,[3] the ratio of the intensity of the rays scattered at 40° to that at 140° should be about 1.10. But their experimental ratio was 1.04, which differs from our theory by more than their probable experimental error.

It will be remembered, however, that our theory, and experiment also, indicates a difference in the wave-length of the X-rays scattered in different directions. The softer X-rays which are scattered backward are the more easily absorbed and, though of smaller intensity, may produce an

[1] M. Ishino, Phil. Mag. **33**, 140 (1917).
[2] M. Ishino, loc. cit.
[3] Barkla and Ayers, loc. cit.

ionization equal to that of the beam scattered forward. Indeed, if α is small compared with unity, as is the case for ordinary X-rays, Eq. (27) may be written approximately $I_\theta/I_\theta' = (\lambda_0/\lambda_\theta)^3$, where I_θ' is the intensity of the beam scattered at the angle θ according to the classical theory. The part of the absorption which results in ionization is however proportional to λ^3. Hence if, as is usually the case, only a small part of the X-rays entering the ionization chamber is absorbed by the gas in the chamber, the ionization is also proportional to λ^3. Thus if i_θ represents the ionization due to the beam scattered at the angle θ, and if i_θ' is the corresponding ionization on the classical theory, we have $i_\theta/i_\theta' = (I_\theta/I_\theta')(\lambda_\theta/\lambda_0)^3 = 1$, or $i_\theta = i_\theta'$. That is, to a first approximation, the ionization should be the same as that on the classical theory, though the energy in the scattered beam is less. This conclusion is in good accord with the experiments which have been performed on the scattering of ordinary X-rays, if correction is made for the excess scattering which appears at small angles.

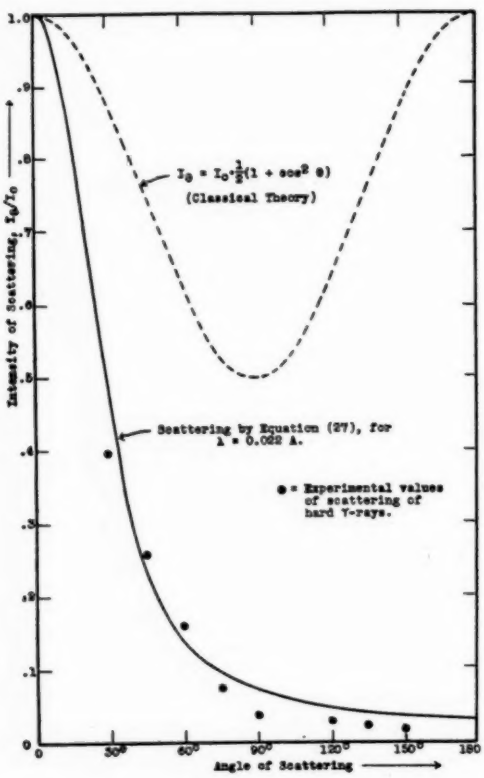

Fig. 7. Comparison of experimental and theoretical intensities of scattered γ-rays.

In the case of very short wave-lengths, however, the case is different. The writer has measured the γ-rays scattered at different angles by iron, using an ionization chamber so designed as to absorb the greater part of even the primary γ-ray beam.[1] It is not clear just how the ionization due to the γ-rays will vary with the wave-length under the conditions of the experiment, but it appears probable that the variation will not be great. If we suppose accordingly that the ionization measures the intensity of the scattered γ-ray beam, these data for the intensity are represented by the circles in Fig. 7. The experiments showed that the intensity at 90° was 0.074 times that predicted by the classical theory, or 0.037 I_0, where I_0 is the intensity of the scattering at the angle $\theta = 0$ as calculated on either the classical or the quantum theory. The absolute intensities of the scattered beam are accordingly plotted using I_0 as the unit. The solid curve shows the intensity in the same units, calculated according to Eq. (27). As before, the wave-length of the γ-rays is taken as 0.022 A. The beautiful agreement between the theoretical and the experimental values of the scattering is the more striking when one notices that there is not a single adjustable constant connecting the two sets of values.

Discussion

This remarkable agreement between our formulas and the experiments can leave but little doubt that the scattering of X-rays is a quantum phenomenon. The hypothesis of a large electron to explain these effects is accordingly superfluous, for all the experiments on X-ray scattering to which this hypothesis has been applied are now seen to be explicable from the point of view of the quantum theory without introducing any new hypotheses or constants. In addition, the present theory accounts satisfactorily for the change in wave-length due to scattering, which was left unaccounted for on the hypothesis of the large electron. From the standpoint of the scattering of X-rays and γ-rays, therefore, there is no longer any support for the hypothesis of an electron whose diameter is comparable with the wave-length of hard X-rays.

The present theory depends essentially upon the assumption that each electron which is effective in the scattering scatters a complete quantum. It involves also the hypothesis that the quanta of radiation are received from definite directions and are scattered in definite directions. The experimental support of the theory indicates very convincingly that a radiation quantum carries with it directed momentum as well as energy.

Emphasis has been laid upon the fact that in its present form the

[1] A. H. Compton, Phil. Mag. **41**, 758 (1921).

quantum theory of scattering applies only to light elements. The reason for this restriction is that we have tacitly assumed that there are no forces of constraint acting upon the scattering electrons. This assumption is probably legitimate in the case of the very light elements, but cannot be true for the heavy elements. For if the kinetic energy of recoil of an electron is less than the energy required to remove the electron from the atom, there is no chance for the electron to recoil in the manner we have supposed. The conditions of scattering in such a case remain to be investigated.

The manner in which interference occurs, as for example in the cases of excess scattering and X-ray reflection, is not yet clear. Perhaps if an electron is bound in the atom too firmly to recoil, the incident quantum of radiation may spread itself over a large number of electrons, distributing its energy and momentum among them, thus making interference possible. In any case, the problem of scattering is so closely allied with those of reflection and interference that a study of the problem may very possibly shed some light upon the difficult question of the relation between interference and the quantum theory.

Many of the ideas involved in this paper have been developed in discussion with Professor G. E. M. Jauncey of this department.

WASHINGTON UNIVERSITY,
SAINT LOUIS,
December 13, 1922

THE CRYSTAL STRUCTURE OF QUARTZ

By L. W. McKeehan

Abstract

Crystal structure of quartz.—Photographs by the powder method of X-ray crystal analysis have confirmed the *space-lattice* proposed by others. A careful study of 30 possible arrangements has shown that the *arrangement of atoms* which best fits the observed intensities of the lines in the pattern differs somewhat from those previously proposed, maintaining more clearly the identity of the molecule SiO_2. These molecules are obtuse-angled isosceles triangles (angle at Si atom-center, 115° 14′; distance between Si and O atom-centers, 1.631×10^{-8} cm) lying in the basal planes of each of three interpenetrating hexagonal space-lattices, so that the crystal may be considered as built up of layers of molecules, much closer together than adjacent molecules in the same layer.

PREVIOUS investigators have shown that the fundamental space-lattice of quartz is hexagonal (Γ_h) and that three molecules SiO_2 are to be associated with each unit of structure (pair of adjacent triangular right prisms, edge of base a, altitude c). A recent theoretical paper by Huggins [1] suggests a simple arrangement of atom-centers consistent with these facts and with the atomic radii for Si and O determined otherwise. Photographs by the powder method of X-ray crystal analysis have been taken, and a search has been made for an atomic arrangement consistent with the observed intensities of the lines in the pattern. The best arrangement differs in some respects from that suggested by Huggins and may prove to be of value in determining the shapes of the component atoms. Study of other crystalline forms of silica has been undertaken to throw additional light on this question.

The most general arrangement consistent with previous data is shown in Fig. 1 which gives two projections of a single unit of structure, outlined in dashes. The upper projection is on the basal plane (00.1)[2] and the lower on one of the lateral planes (01.0). The only elements of symmetry are the digonal rotation-axes, Q_1, Q_2, and Q_3, and the trigonal screw-axes, P_1, P_2, and P_3, the latter having translation-components, $c/3$.

[1] M. L. Huggins, Phys. Rev. (2) **19**, 363–368 (1922).

[2] This notation for indices of form in the hexagonal system avoids including a derived index, the third being always the sum of the first and second with the sign changed. It also eliminates negative indices in the symbols for typical planes; *e.g.*, (01.0) for (01$\bar{1}$0), and sets off the fourth index which is not of the same crystallographic value as the first three. Cf. A. W. Hull and W. P. Davey, Phys. Rev. (2) **17**, 549–570 (1921), on charts only.

The direction of the translation along the screw-axes determines whether the quartz is optically right- or left-handed. In the notation of Hilton [1] the symbol of the space-group is D_3^3 or D_3^5 and the symmetry is that of rhombohedral enantiomorphy in the hexagonal system.

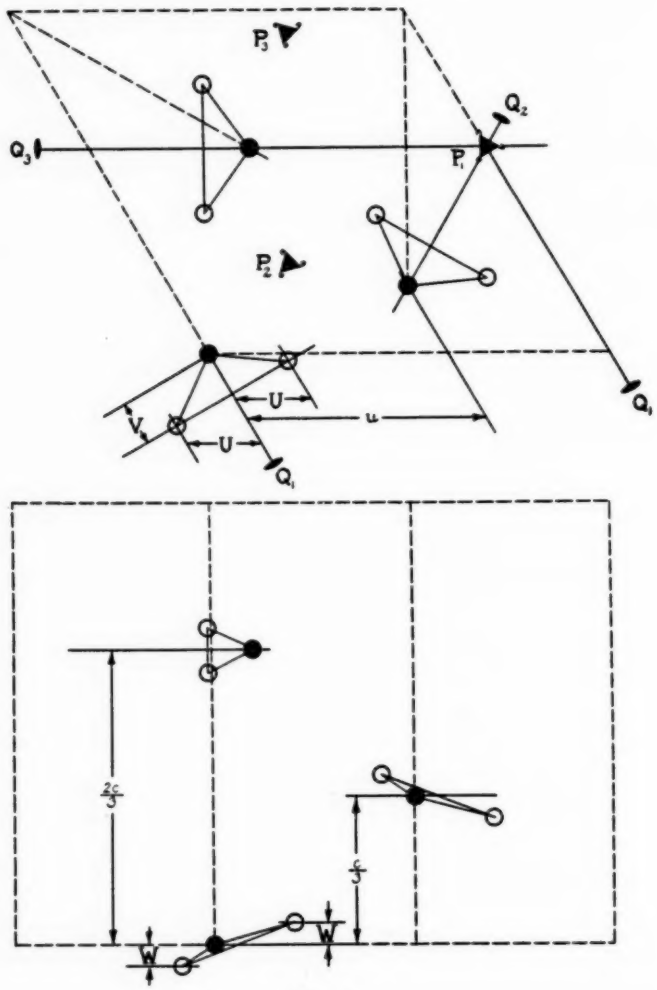

FIG. 1

For convenience in wording, we will speak of a molecule SiO_2, meaning thereby any silicon atom and the two nearest oxygen atoms. This will be ambiguous only in case more than two oxygen atoms are equally near, and in that case we will arbitrarily regard as a molecule any silicon atom and the two nearest oxygen atoms which lie nearest to the basal plane (00.1) through its center.

[1] H. Hilton, Mathematical Crystallography, Oxford (1903).

The symmetry of the crystal now requires that:

(*a*) In each molecule the two O-atom-centers are equidistant from the Si-atom-center, so that the three atom-centers determine an isosceles triangle.

(*b*) Each Si-atom-center is equidistant from two O-atom-centers in adjacent molecules, the Si-atom-centers of which belong to different space-lattices from each other and from that of the Si-atom-center under consideration.

The special additional assumptions made by Huggins may be expressed in various ways. The reason for the choice here made will be evident when the experimental result is discussed. They are as follows:

(*c*) Each O-atom-center is equidistant from two Si-atom-centers, and the plane determined by these three points cuts the basal plane (00.1) of the space-lattice of one of its Si-atom-centers in one of its principal rows of points.

(*d*) The distance between the members of any adjacent pair of unlike atom-centers is 1.82×10^{-8} cm.

These assumptions completely fix the positions of both Si- and O-atom-centers for any particular values of the space-lattice parameters a and c. The values of a and c quoted by Huggins are due to the Braggs,[1] and are $a = 4.89 \times 10^{-8}$ cm, $c = 5.375 \times 10^{-8}$ cm. It is not at all difficult to compute the coördinates of the atom-centers and the angles between lines joining any atom-center to its neighbors. The following table gives the results of such calculations.

TABLE I

Crystal Constants Computed on Huggins' Assumptions

$a = 4.89 \times 10^{-8}$ cm, $\quad c = 5.375 \times 10^{-8}$ cm.

Coördinates of atom-centers, grouped by molecules.

Si [0, 0, 0]
O [0.381a, 0.025a, 0.041c][− 0.381a, − 0.356a, − 0.041c]

Si [0.591a, 0.182a, 0.333c]
O [0.566a, 0.538a, 0.374c][0.947a, 0.157a, 0.292c]

Si [0.409a, 0.591a, 0.667c]
O [0.053a, 0.210a, 0.708c][0.434a, 0.972a, 0.626c]

Angles at atom-centers between lines to adjacent atom-centers

At Si between lines to O of same molecule	127° 10′
At Si between lines to O of adjacent molecules	121° 09′
At O between lines to Si of same molecule and Si of adjacent molecule	118° 27′

Distance between Si- and O-atom-centers, either of same or of adjacent molecules, 1.82×10^{-8} cm.

[1] W. H. Bragg and W. L. Bragg, X-Rays and Crystal Structure, London (1915).

The approximate relative intensities of the various possible reflections can be computed for any proposed arrangement of atoms by the formulæ

$$I = md^3(A^2 + B^2),$$
$$A = \sum_p \rho_p \cos 2\pi(hx_p + ky_p + lz_p),$$
$$B = \sum_p \rho_p \sin 2\pi(hx_p + ky_p + lz_p),$$

wherein h, k, l are the Miller indices of the reflecting planes (multiplied by the order of reflection), m is the number of families of such planes, d is the perpendicular distance between adjacent planes (divided by the order of reflection), ρ_p is the scattering power of the atom p, which has the coördinates x_p, y_p, z_p, in terms of the three principal parameters (in this case a, a, c). The values of ρ_p are in this case assumed to be the same for silicon with four electrons removed, and oxygen with two electrons added, it being thought reasonable to assume that the molecule SiO_2 is held together by the powerful electric forces which this exchange of electrons would create. The equations given above differ from those of Wyckoff [1] only by the factor md in the first formula, which takes care of the special circumstances of the powder method. The testing of any proposed arrangement consists then in the computation of I for the first few reflections, corresponding to the largest values of d, and a comparison with the relative intensities actually observed in the photographs. The values of I are surprisingly sensitive to small changes in the coördinates of the atom-centers.

In seeking a suitable arrangement, conditions (a) and (b) must of course be retained, so that the twenty-four coördinates of atom-centers not at the origin are by no means independent. There are, however, four variables at disposal, u, U, V, W in Fig. 1. The ranges in the values of these variables which have been examined cover the arrangements which do not put two oxygen atom-centers closer together than 1.30×10^{-8} cm, which appears to be a fair minimum value for the diameter of an oxygen atom. The arrangements tested included, of course, that proposed by Huggins. No attempt was made to locate the atom-centers with great apparent accuracy, since the number of uncertain factors, both theoretical and experimental, makes additional accuracy largely illusory. About thirty cases were worked out completely enough to check with the first six possible reflections. The best fit with the observed intensities was found for the values of coördinates given in Table II., and variations of as little as $0.02a$ or $0.02c$ from the preferred values make even the order of intensities different from that observed, so that the probable errors in the coördinates are thought to be somewhat less than this in magnitude.

[1] R. W. G. Wyckoff, Am. J. Sci. **50**, 317–360 (1920).

The parameters of the space-lattice determined from the positions of the lines differ so little from the Braggs' values that it would be merely confusing to substitute new values. The values of a and c used in Table I. have accordingly been used in computing the lower half of Table II.

TABLE II

Crystal Constants from These Experiments

$a = 4.89 \times 10^{-8}$ cm, $\quad c = 5.375 \times 10^{-8}$ cm.

Coördinates of atom-centers, grouped by molecules.

Si [0, 0, 0]
O [0.325a, − 0.016a, 0][− 0.325a, − 0.341a, 0]

Si [0.603a, 0.206a, 0.333c]
O [0.619a, 0.547a, 0.333c][0.944a, 0.222a, 0.333c]

Si [0.397a, 0.603a, 0.667c]
O [0.056a, 0.278a, 0.667c][0.381a, 0.928a, 0.667c]

Angles at atom-centers between lines to adjacent atom-centers

At Si between lines to O of same molecule	115° 14′
At Si between lines to O of adjacent molecules	111° 28′
At O between lines to Si of same molecule and Si of adjacent molecule	137° 50′

Distance between Si- and O-atom-centers

Of same molecule	1.631 × 10^{-8} cm
Of adjacent molecules	2.176 × 10^{-8} cm

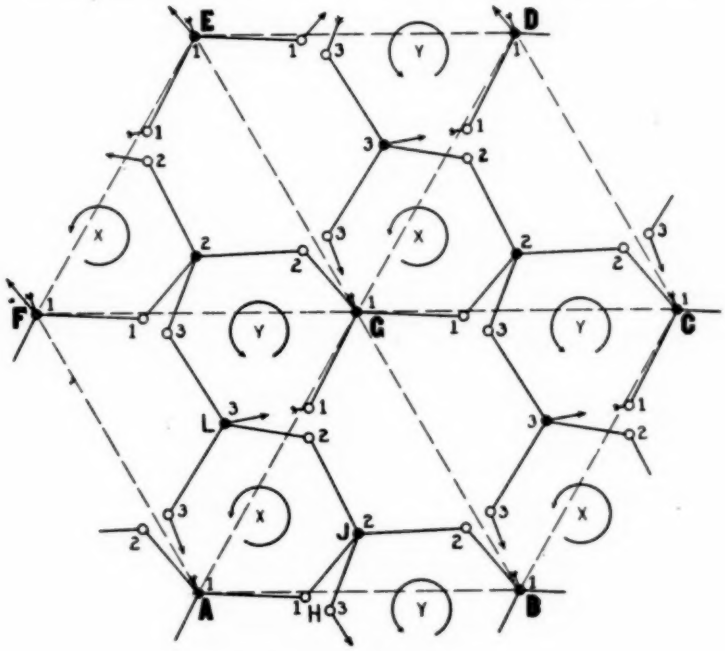

Fig. 2

The arrangement described in Table II. is illustrated in Fig. 2 which gives a projection of atom-centers on a basal plane and three projections of a unit of structure with the atoms represented by opaque spheres of arbitrary sizes. The lettering and numbering corresponds with that in Fig. 2 of Huggins' paper, with which it should be compared. It should be noted, however, that his preferred arrangement does not give oxygen atoms at different levels the same x and y coördinates, as shown by his figure here referred to. A striking peculiarity of the arrangement here proposed is the maintenance of identity of groups SiO_2 lying in basal planes. The crystal can be considered as built up of layers of molecules with their planes perpendicular to the hexagonal axis, so spaced, however, that adjacent layers are much closer together than adjacent molecules in the same layer.

It is interesting to compare the elbow-shaped molecule SiO_2, thus indicated, with the molecule CO_2, with which analogies might be expected. According to Rankine [1] the molecule CO_2 possesses symmetry about an axis and would therefore be expected to have relatively weak stray fields for maintenance of condensed phases. An irregular shape, even in cases of chemical saturation where symmetry is theoretically possible, thus appears able to prevent volatility in the case of the refractory SiO_2. Reëstablishment of symmetry in silicane, SiF_4, recently investigated by Rankine and Smith,[2] restores the low boiling point.

RESEARCH LABORATORIES OF THE
AMERICAN TELEPHONE AND TELEGRAPH COMPANY
AND THE WESTERN ELECTRIC COMPANY, INCORPORATED.
November 3, 1922

[1] A. O. Rankine, Roy. Soc., Proc. A **98**, 369–374 (1921).
[2] A. O. Rankine and C. J. Smith, Phys. Soc., Proc. **34**, 181–186 (1922).

ELECTRONIC STRUCTURES OF THE SPINELS

By Maurice L. Huggins

Abstract

Crystal structure of the spinels.—(1) The most probable *arrangement of valence electrons* is that in which there is a pair on or near each centerline between adjacent atoms. The valence shell of each oxygen and divalent metal atom is a tetrahedron of electronpairs; that of each trivalent metal atom is an octahedron of pairs. (2) *The distances between adjacent atomic centers* are calculated (from the densities) and the *positions of the oxygen centers* determined in crystals of $ZnAl_2O_4$, $ZnCr_2O_4$, $ZnFe_2O_4$, $MgAl_2O_4$, $MgCr_2O_4$, $MnAl_2O_4$, $MnCr_2O_4$, $CdCr_2O_4$, and $FeFe_2O_4$ by means of the assumptions that the Zn–O distance in the first three equals that in ZnO and that corresponding interatomic distances in different spinels are equal. (3) *Densities of* $MgFe_2O_4$ *and* $MnFe_2O_4$ are computed to be 4.47 and 4.90 gm/cm^3, respectively, on the basis of these same assumption. (4) *Chemical formulæ.* There is no physical basis in the arrangement of atoms and electrons for the formulæ $R''O \cdot R_2'''O_3$ or $R''(R'''O_2)_2$.

Atomic radii of divalent Zn, Fe, Mg, Mn, and Cd and of trivalent Al, Cr, and Fe are computed (Table III.), assuming the radius of oxygen to be 0.65 A.

Association of ferromagnetism with a particular distribution of electrons, such as a concentration of triplets in the same end of the kernel of each trivalent iron atom (in a fully magnetized crystal), is suggested.

Arrangement of the atoms.—The group of minerals known as the spinels, the general formula of which is $R''R_2'''O_4$, R″ being a divalent metal (Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb) and R‴ a trivalent metal (Al, Cr, Fe, Co), has been studied by means of x-rays by W. H. Bragg,[1] Nishikawa,[2] and Vegard.[3] According to their results, the R″ atoms are at the points of a "diamond type" of structure (Fig. 1), the other atoms being distributed around these as indicated in Figs. 2 and 3. Each R″ atom is surrounded by four equidistant, tetrahedrally disposed oxygen atoms. Around each R‴ atom are six oxygen atoms, at the corners of an octahedron. Each oxygen atom is surrounded by three equidistant R‴ atoms and one R″ atom.

Arrangement of electrons.—According to the Lewis theory of atomic structure [4] and the author's extension of it to the heavy elements,[5] there

[1] W. H. Bragg, Phil. Mag. **30**, 305 (1915).
[2] Nishikawa, Math. Phys. Soc. Tokyo **8**, 199 (1915).
[3] Vegard, Phil. Mag. **32**, 65 (1916).
[4] G. N. Lewis, J. Am. Chem. Soc. **38**, 762 (1916).
[5] Huggins, Science **55**, 459 (1922); J. Phys. Chem. **26**, 601 (1922).

are six valence electrons per oxygen atom, two per R″ atom, and three per R‴ atom, a total of 32 per "molecule." This is exactly the number required to form a tetrahedron of electronpairs, a stable "group of eight" or "octet," around each oxygen kernel. Since in every other oxygen-containing crystal studied there is a similar tetrahedron of pairs

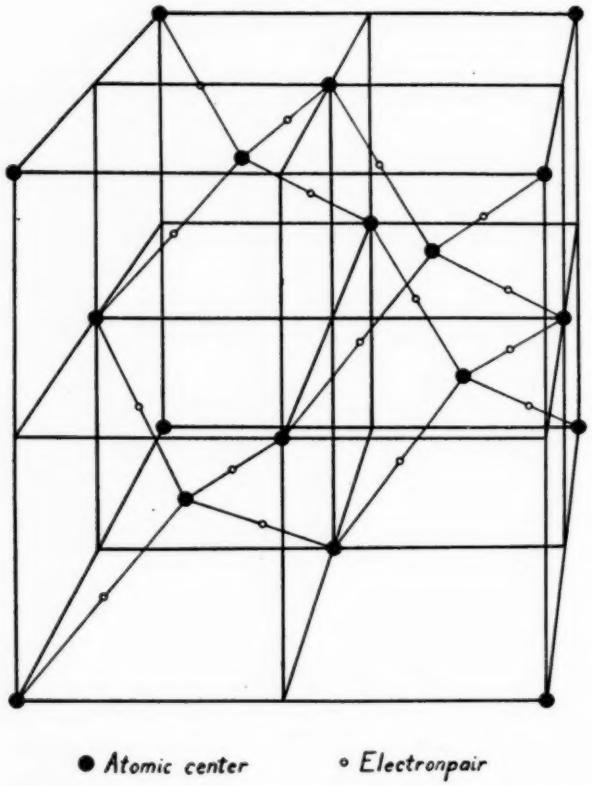

Fig. 1. Arrangement of atomic centers and valence electronpairs in the unit cube of the diamond crystal.

around each oxygen kernel, we may assume that to be the case in these crystals, if such an assumption leads to a structure which is otherwise reasonable. These valence tetrahedra may be oriented in either of three ways in accord with the threefold symmetry about the *R″–O* centerlines. Two of these orientations give structures quite unlike those which other crystals have been found to possess. If the third is correct, each electron-pair is on (or very near) the centerline between an oxygen and one of the four surrounding atoms. Such an arrangement is in full accord with the author's theory, which has been fully verified in other crystals,[1]

[1] Huggins, J. Am. Chem. Soc. **44**, 1841 (1922); Phys. Rev. **19**, pp. 346, 354, 363, 369 (1922); **21**, 379 (1923).

that the valence electrons tend to be in pairs on or near the centerlines between adjacent atoms [1] and opposite the faces of the polyhedra formed by the outermost electronpairs or triplets in the kernels of the atoms thus joined.[2]

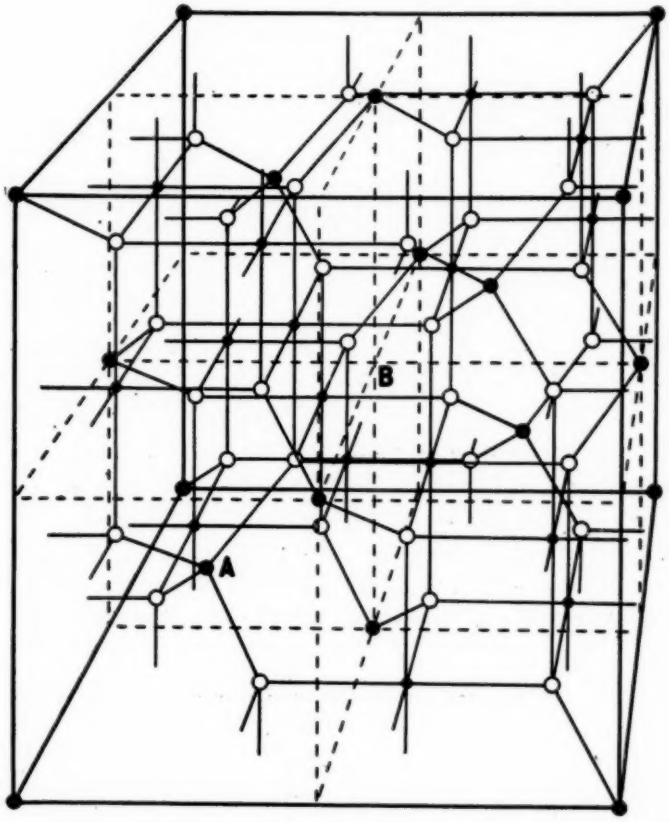

Fig. 2. Arrangement of atomic centers in a unit cube of a spinel crystal.
●R″, ●R‴, ○O.

The probable atomic formulæ of the metals concerned, according to the author's theory, are given in Table I. The first parenthesis in each represents the nucleus and each succeeding parenthesis an atomic shell, in order from the nucleus out, the number of electrongroups and the number of electrons in each group being given for each shell except the last or valence shell.[3] The outermost kernel shell in each of the

[1] Exceptions to this tendency are found in the alkali halides, the alkaline earth oxides and sulfides, the metals, and a few other crystals.

[2] In an electropositive atom a kernel tetrahedron is sometimes surrounded by a valence *octahedron*. Cf. Huggins, Phys. Rev. **19**, 354 (1922).

[3] For the derivation of these structures and the further interpretation of the formulæ, see Huggins, J. Phys. Chem. **26**, 601 (1922).

divalent atoms is a tetrahedron, and the valence shell is a tetrahedron (one pair opposite each face of the kernel shell), if the structure assumed in the preceding paragraph is correct. The outermost kernel shell of each trivalent atom is a (distorted) cube or a tetrahedron; and the valence shell, in these crystals, is an octahedron.

TABLE I

Mg	$(+12)(2\times1)(4\times2)(2)$
Mn	$(+25)(2\times1)(1\times3+5\times2)(4\times2)(2)$
Fe	$(+26)(2\times1)(2\times3+4\times2)(4\times2)(2)$
Co	$(+27)(2\times1)(3\times3+3\times2)(4\times2)(2)$
Ni	$(+28)(2\times1)(4\times3+2\times2)(4\times2)(2)$
Cu	$(+29)(2\times1)(5\times3+1\times2)(4\times2)(2)$
Zn	$(+30)(2\times1)(6\times3)(4\times2)(2)$
Cd	$(+48)(2\times1)(8\times3)(6\times2)(4\times2)(2)$
Pb	$(+82)(2\times1)(8\times3)(6\times3)(8\times2)(6\times2)(4\times2)(2)$
Al	$(+13)(2\times1)(4\times2)(3)$
Cr	$(+24)(2\times1)(3\times3+5\times2)(3)$
Fe	$(+26)(2\times1)(5\times3+3\times2)(3)$ or $(+26)(2\times1)(1\times3+5\times2)(4\times2)(3)$
Co	$(+27)(2\times1)(6\times3+2\times2)(3)$ or $(+27)(2\times1)(2\times3+4\times2)(4\times2)(3)$

The positions of the oxygen centers.—With the atomic marshalling found for the spinels, it is impossible that the tetrahedron of electron-pairs around each oxygen kernel should be a *regular* tetrahedron, and at the same time that the octahedron of pairs around each R‴ kernel should be a *regular* octahedron. If the former were the case, the R″–O distance would be just two thirds AB (Fig. 3); if the latter, it would be

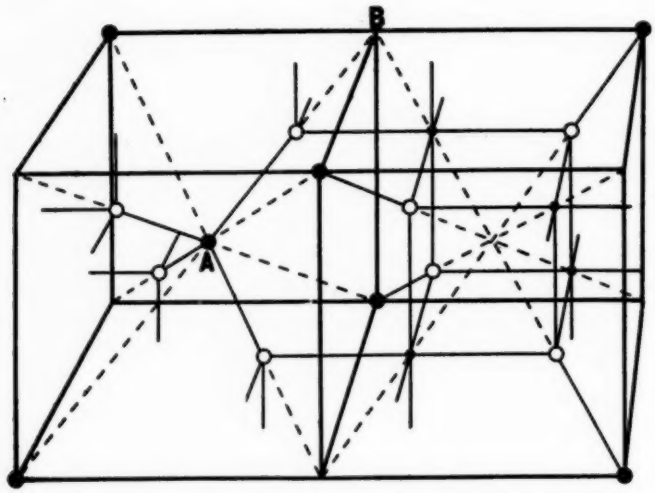

Fig. 3. Arrangement of atomic centers within two of the eighth-unit cubes of a spinel crystal. ●R″, ●R‴, ○O.

exactly half AB [1] (assuming throughout that the valence pairs are *on the centerlines* between atoms). Actually we should expect R″–O to be intermediate between 0.500 AB and 0.667 AB, and we shall see that this is the case. For simplicity in making the figures, perfect octahedra have been assumed, R″–O being taken equal to one half AB.

Experimentally, by considering the relative intensities of the different orders of x-ray reflection from various crystal faces, Bragg found that in magnetite, $FeFe_2O_4$, the oxygen centers are *roughly* half-way between cube centers and cube corners. In spinel, $MgAl_2O_4$, his experiments indicated that the R″–O distance is slightly greater. Nishikawa estimated R″–O/AB as about 0.54 in spinel and between 0.50 and 0.53 in magnetite.

It will now be shown how the oxygen positions can be more accurately obtained in an entirely different way.

In a crystal of $ZnFe_2O_4$, $ZnAl_2O_4$, or $ZnCr_2O_4$, each zinc atom is bonded by single bonds to four tetrahedrally disposed oxygen atoms, and each oxygen atom to four metal atoms, at tetrahedron corners. This disposition is essentially the same as that in a crystal of ZnO, hence we may be quite sure that the distance between zinc and oxygen centers is practically the same in each of these crystals. If we assume this, the position of each oxygen center relative to the surrounding atoms is determined. From the dimensions of the unit cells calculated from the densities, the Cr–O, Al–O and Fe–O distances may then be easily obtained.

Then, assuming the Cr–O distance to be the same in the chromites of magnesium, manganese, and cadmium as in $ZnCr_2O_4$, and the Fe‴–O distance to be the same in $FeFe_2O_4$ as in $ZnFe_2O_4$, the R″–O distances in these substances are similarly found (see Table II.). In the magnesium and manganese aluminates, we might either take the Al–O distances calculated for $ZnAl_2O_4$, and from it calculate the R″–O distances, or we might assume the R″–O values calculated for the corresponding chromates, and from them calculate the distance between Al and O centers. The latter procedure is probably the better of the two, since the Al–O distances computed through the Mg and Mn compounds check much more closely with each other than with that computed for $ZnAl_2O_4$, and since the density given for the latter compound is probably not very accurate. (If the Al–O distance in $ZnAl_2O_4$ were 1.915 A, as calculated for $MnAl_2O_4$, Zn–O being 1.960 A, the density would be 4.550 rather than 4.58 gm/cm³.)

[1] Symmetry considerations place the centers of the R‴ atoms on the small cube diagonals at about half the distance between the cube centers and the cube corners. They would be *exactly* in these positions if their kernels possessed cubic or octahedral symmetry. For our present purposes we shall assume them to be so situated.

TABLE II

Formula	Density [1] (gm/cm³)	Edge of unit cube	R″–O	R‴–O	R″–O/*AB*
$ZnCr_2O_4$	5.30	8.34A	1.96*A	2.00A	.54
$ZnAl_2O_4$	4.58	8.09	1.96*	1.89	.56
$ZnFe_2O_4$	5.33	8.42	1.96*	2.03	.54
$MgCr_2O_4$	4.415	8.32	1.94	2.00*	.54
$MgAl_2O_4$	3.57	8.08	1.94*	1.92	.56
$MgAl_2O_4$	3.59[2]	8.06[2]	1.94*	1.91	.56
$MgFe_2O_4$	4.47[3]	8.39[3]	1.94*	2.03*	.54
$MnCr_2O_4$	4.87	8.45	2.04	2.00*	.56
$MnAl_2O_4$	4.12	8.22	2.04*	1.91	.57
$MnFe_2O_4$	4.90[3]	8.53[3]	2.04*	2.03*	.55
$CdCr_2O_4$	5.79	8.61	2.16	2.00*	.58
$FeFe_2O_4$	5.23	8.36	1.92	2.03*	.53
$FeFe_2O_4$	5.16[2]	8.40[2]	1.95	2.03*	.54

* Assumed.

Good density data for the ferrites of magnesium and manganese are not available. However, by assuming the interatomic distances in these compounds to be the same as the corresponding distances in other spinels, we can compute them to be 4.47 and 4.90 gm/cm³, respectively.

In the last column of Table II. are given the values of the ratio R″–O/*AB* for each of these crystals. This ratio is in each case between one half and two thirds (as was predicted before the computation was made).

Atomic radii.—In Table III. are given the atomic radii of the various elements present in these crystals, calculated from the R–O distances on the assumption that the oxygen radius (the distance from atomic center to valence electronpair) is 0.65 A.[4] Should this value prove to be lower than the true value, the radii calculated for the other elements in the

TABLE III

Atomic Radii

$(O^{+6})(4 \times 2)(4\ R)$	0.65A
$(Zn^{+2})(4 \times 2)(4\ O^{+6})$	1.31
$(Fe^{+2})(4 \times 2)(4\ O^{+6})$	1.27–1.30
$(Mg^{+2})(4 \times 2)(4\ O^{+6})$	1.29
$(Mn^{+2})(4 \times 2)(4\ O^{+6})$	1.39
$(Cd^{+2})(4 \times 2)(4\ O^{+6})$	1.51
$(Fe^{+3})(6 \times 2)(6\ O^{+6})$	1.38
$(Al^{+3})(6 \times 2)(6\ O^{+6})$	1.26
$(Cr^{+3})(6 \times 2)(6\ O^{+6})$	1.35

[1] From Groth's Chemische Krystallographie, Vol. II. (Engelmann, Leipzig, 1908), except as otherwise noted.

[2] Calculated from the "chamber angles" given by W. H. Bragg and W. L. Bragg in "X Rays and Crystal Structure," G. Bell and Sons, London, 1916, p. 172.

[3] Calculated from the assumed R″–O and R‴–O distances.

[4] Huggins, Phys. Rev. **21**, 205 (1923); W. L. Bragg, Phil. Mag. **40**, 169 (1920), also gives this value for the oxygen radius.

table are correspondingly higher than the true distances, and vice versa. The accuracy of these radii values, except those for oxygen and zinc, depends largely on the accuracy of the values of the densities used, hence if any of the latter are later found to be much in error, the radii calculated therefrom will be correspondingly in error.

It is worthy of note that the radius of the iron atom is by no means the same when the kernel has a net charge of + 2 and is surrounded by *four* electronpairs as when the kernel has a charge of + 3 and is surrounded by *six* valence pairs.

The correct formula for the spinels.—In the arrangement pictured in Figs. 2 and 3 and described in the preceding pages, the atoms are obviously not divided into R″O and $R_2'''O_3$ groups, nor into R″ and $R'''O_2$ ions. The whole crystal is a single molecule, each atom being held by single bonds to those adjacent. Hence the empirical formula $R''R_2'''O_4$ is the only one which correctly represents the structure of these substances in the crystalline state.

Ferromagnetism.—The electronic structures of these crystals and of their component atoms suggest a possible partial explanation of the cause of ferromagnetism.

Atoms of chromium, manganese, iron, cobalt, and nickel each possess a kernel shell, according to the author's theory, containing *both* pairs and triplets of electrons. In general, we should not expect electrons to shift from one electrongroup to another (thereby changing the distribution of pairs and triplets) in an atom in a crystal, but in some crystals this might be possible. Ferromagnetism in iron, magnetite, etc., then, might be the result of a concentration of electron *triplets* in the *same* end of each atomic kernel (or at least in a large number of them), somewhat as shown

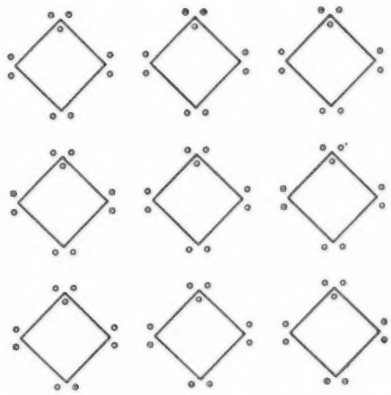

Fig. 4. Illustrating the electron arrangement in a hypothetical fully-magnetized two-dimensional crystal.

in Fig. 4 for an imaginary two-dimensional crystal. In magnetite it is probably the trivalent atoms which can assume this regular orientation, for the other ferrites (of Mg, Mn, Co, Ni, Cu, Zn, Pb) are ferro-magnetic, while ferrous aluminate and chromite are not so.

Why an unsymmetrical distribution of electrons in an atom should give it magnetic properties is not now evident. The writer hopes at a later date, however, to be able to present a more complete theory.

This paper is the result of work at the University of California begun while the author was holder of a Du Pont Fellowship in Chemistry and completed while a National Research Fellow. Grateful acknowledgment is given of the aid afforded by these fellowships.

CHEMICAL LABORATORY,
HARVARD UNIVERSITY,
November 1, 1922

THE MOTION OF ELECTRONS IN CARBON MONOXIDE

By H. B. Wahlin

Abstract

Motion of electrons in carbon monoxide.—*Formation of negative CO ions* was found, in previous mobility experiments, to be extremely rare. This result has now been verified with CO generated by formic acid dripping into concentrated sulphuric acid and purified with great care. The very high mobilities obtained indicate clearly that an electron liberated in pure CO remains free. *Electron mobility as a function of field and pressure* was studied using alternating potentials with frequencies up to 340,000 cycles, generated by a vacuum tube oscillating circuit. At a pressure of 723 mm a mobility of 118 m/sec/volt/cm was measured, which decreased to 81.5 m as the field intensity increased from 4.5 to 48 volts/cm. The Townsend-Compton theory of mobility leads to the following equation for the speed of an electron in a field x: $v = a(x/p)/\sqrt{B + (x/p)}$. This leads to a relation between frequency and critical value of the field X_1 which is found to agree with the results for CO if $a = 1.87\ (10)^6$ and $B = .005$, the pressure being in mm Hg. This agreement suggests (1) that the mean free path is independent of the field, and (2) that the electron collisions with CO molecules are very inelastic.

IN an earlier article [1] measurements of mobilities were reported which showed that only rarely does an electron attach itself to a molecule of carbon monoxide. In fact, it was found that on the average, the electrons make 10^8 impacts before uniting to form a negative ion, and mobilities as high as 240 cm/sec/volt/cm were obtained at atmospheric pressure.

In a determination of this kind, however, the presence in the gas of a small amount of impurity could alter the results appreciably, especially if the impurity were of an electronegative character, because the electrons show a greater tendency to unite with electronegative substances than with others. It was necessary, therefore, that extreme precautions be taken in generating and purifying the gas, not only to eliminate impurities as far as possible, but also to limit the kinds of impurities which could possibly be present. It was in order to determine whether, when a different method was used in generating the carbon monoxide, results differing from those given above would be obtained, that the following experiments were undertaken.

In the previous work, the carbon monoxide was generated through the action of concentrated sulphuric acid on sodium-formate. This method

[1] H. B. Wahlin, Phys. Rev. **19**, p. 173 (1922).

was found to be unsatisfactory, however, due to the fact that the evolution of gas was difficult to control. In these later experiments formic acid was substituted for the sodium-formate. The formic acid was allowed to drip into the concentrated sulphuric acid and by varying the rate of drip, the rate of evolution of the gas could be controlled at will.

From the generator the gas passed through a solution of potassium hydroxide to remove any sulphur dioxide and sulphur trioxide fumes which might be given off from the sulphuric acid during the reaction. This would also remove any formic acid vapors that might be carried over. Next the gas passed over calcium chloride to dry it partially and then through a tube containing hot copper which had first been reduced by hydrogen. At this stage any oxygen present in the gas would unite with the carbon monoxide molecules to form carbon dioxide. In order to remove this, the gas passed through a tower about 75 cm high, containing glass beads and a solution of potassium hydroxide. The glass beads served to break up the bubbles of gas and to retard their progress through the solution. The gas next passed through a tube about 75 cm long, containing solid potassium hydroxide, and then through a similar tube containing calcium chloride. It next passed over phosphorous pentoxide to complete the drying, through a trap and a spiral both cooled to liquid air temperature, and into the chamber in which the measurements were made. The gas was generated as slowly as possible so that its passage through the purification system took some time. In making a filling, the chamber was washed out by exhausting to a pressure of 1 mm of mercury or less and filling it to atmospheric pressure. This was repeated four or five times in succession so that the residual gas from the preceding fillings was small.

At the outset of the experiment the carbon monoxide was allowed to remain in the chamber for several days without any data being taken. This served to remove such impurities as might gradually diffuse into the chamber from the walls. When readings finally were taken, it was found that the results were not altered by allowing the gas to remain in the chamber for twenty-four hours, and since the set of readings taken on one filling of gas in no case extended over a period of more than twelve hours, any effect due to contamination from the walls was negligible.

In the early part of this work the method of procedure in making the measurements was similar to that used in the original experiments. The mobility, determined by using the Rutherford square wave alternating potential method, now came out as high as 800 cm/sec/volt/cm at atmospheric pressure. However, with these high values for the

mobility and with the limited range of frequencies obtainable with a commutator, the intercept of the mobility curve on the voltage axis was only one or two volts so that an error of a fraction of a volt in determining this intercept would alter the results appreciably.

In order to obtain frequencies such that the voltage intercepts of the mobility curves could be obtained as a function of the frequency for a much greater range of frequencies, the commutator was replaced by a vacuum tube oscillating circuit of the Hartley type, Fig. 1. For fre-

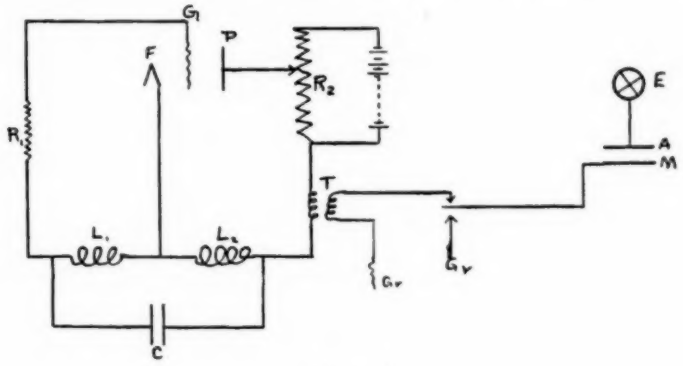

Fig. 1

quencies below 80,000 cycles, a high frequency transformer T was included in the plate circuit and the alternating potential was obtained from the secondary of this. For higher frequencies, since the transformer failed to transmit them, it was removed and the alternating potentials were obtained from the condenser C in the oscillating circuit. Results obtained in this way for frequencies below 80,000 cycles checked those obtained when the transformer was used.

One side of the secondary of the transformer was grounded and the other side was connected through a charge and discharge key to the brass plate M which together with the brass plate A was contained in the measuring chamber. The distance between M and A was 16 mm. The electrons were obtained photoelectrically from the plate M. In order to minimize the photoelectric emission from the plate A due to scattered light, this plate was coated with a layer of copper oxide by immersing it in an ammoniacal solution of copper carbonate and then heating the plate to redness in air. The alternating potential was varied by changing the potential of the plate P of the vacuum tube by means of the potential dividing rheostat R_2 and was measured by means of an electrostatic voltmeter. Then by noting the rate of deflection of the electrometer E, due to the charge received by A for various values of

the alternating potential, mobility curves were obtained, and from the intercept of these curves on the voltage axis approximate values of the mobility were calculated from the relation

$$K = \frac{\pi n d^2}{\sqrt{2}\, v}, \tag{1}$$

where d is the distance between the plated M and A, n is the frequency and v is the effective voltage of the intercept of the mobility curve, corrected for the change in potential of the plate A when a potential is applied to M.

Mobility curves were taken with intercepts ranging from 5 volts to 100 volts and at pressures ranging from 100 to 723 mm of mercury.

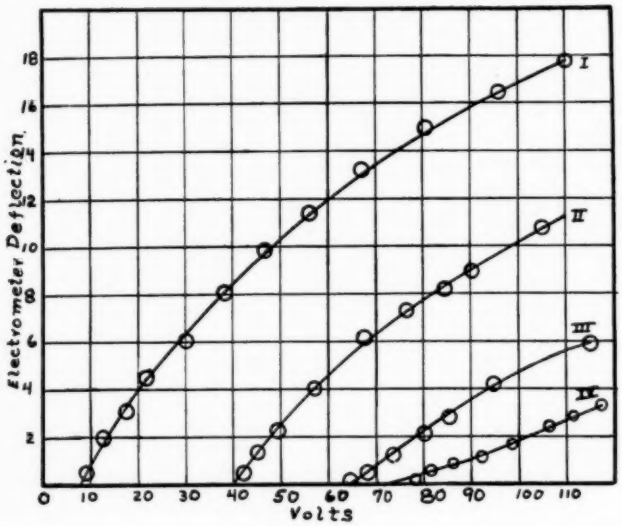

Fig. 2

Fig. 2 illustrates the types of curves obtained at a pressure of 723 mm for different frequencies. At the higher voltages (as may be seen from Curve IV.) the intercepts of these curves become less well defined and the curves show a tendency to approach the voltage axis asymptotically. Loeb [1] found the same thing to be true in his work on nitrogen and has suggested as a possible explanation that it might be due to the presence of impurities in the gas. If a small portion of the electrons become attached to molecules of the gas or impurity they would remain in the space between the plates and might under a space charge action gradually drift across to the upper plate. This effect disappeared in the case of carbon monoxide as the pressure was reduced, as might be expected on

[1] Leonard B. Loeb, Phys. Rev. (Jan., 1922).

the basis of Loeb's explanation, for the probability that an electron will become attached is then decreased.

The values of the mobility, for the curves of Fig. 2, as calculated from Eq. (1) are as follows:

Curve	v (corrected)	n	d	K
I.....	7.2	15,030	16 mm	11,800
II.....	38.0	63,025	" "	9,300
III.....	61.7	94,340	" "	8,700
IV.....	76.0	108,700	" "	8,150

It is to be noted that the mobility is higher for the low fields than for the high ones. For this reason values calculated on the basis of Eq. (1) must be considered as approximate only.

For the case of a sinusoidal alternating potential, Eq. (1) is derived from the expression

$$\frac{dy}{dt} = K\frac{V}{d}\sin 2\pi nt = KX \sin 2\pi nt = Kx, \tag{2}$$

where dy/dt is the velocity of the electron in the direction of the field and x is the instantaneous value of the field intensity whose maximum is X. It is here assumed that K is independent of the field intensity and pressure. In the more general case where this is not so, Eq. (2) becomes

$$dy/dt = f(x, p)X \sin 2\pi nt.$$

For the case where the electrons just succeed in reaching the collecting plate during one half cycle of the alternating potential, that is for the case corresponding to the intercept of the mobility curve on the voltage axis, we get

$$d = \int_0^{\frac{1}{2n}} f(x, p)X_1 \sin 2\pi nt\, dt,$$

where X_1 is the value of the field corresponding to the intercept.

As may be seen from this equation, unless the form of the function $f(x, p)$ is known, an exact experimental determination of the mobility of the electron is impossible if a sine wave alternating potential is used.

Substituting for x its value in terms of X, placing $2\pi nt$ equal to θ and solving for n, we get

$$n = \frac{X_1}{2\pi d}\int_0^{\pi} f(p, X_1 \sin\theta)\sin\theta\, d\theta. \tag{3}$$

From this we see that the form of the function must be such that the values of n calculated from this equation shall satisfy the experimental relations between n, X_1 and p.

Determination of $f(x, p)$.—Compton [1] has shown that if an electron loses a fraction q of its energy at each impact, the terminal energy W due to a field x is given by

$$W = 0.575\, xe\lambda/\sqrt{q}. \tag{4}$$

Furthermore, Townsend [2] gives as the expression for the mobility of an electron

$$K = .815\, e\lambda/m\bar{c}, \tag{5}$$

where λ is the mean free path and $\bar{c}$ is the mean velocity of agitation of the electrons. This velocity will be made up of two parts, first, that due to the velocity of agitation in equilibrium with the molecules when the field is zero, and second, the velocity of agitation due to the energy gained in the field. Applying this condition and combining Eqs. (4) and (5) Loeb [3] has shown that the mobility of the electrons should be given by the expression

$$K = .815\, \frac{e\lambda}{m\bar{c}\sqrt{1 + .575 xe\lambda/mc^2\sqrt{q}}}, \tag{6}$$

where $\bar{c}$ now refers to the velocity of agitation in thermal equilibrium with the molecules when the field is zero.

If it is assumed that λ varies inversely as the pressure, this expression reduces to

$$K = \frac{a}{p\sqrt{B + (x/p)}}. \tag{7}$$

Substituting this in Eq. (3) we get

$$n = \frac{aX_1/p}{2\pi d}\int_0^{\pi} \frac{\sin\theta\, d\theta}{\sqrt{B + (X_1/p)\sin\theta}}.$$

This is an elliptic integral which on reduction gives

$$n = \frac{\sqrt{2}\, a\sqrt{X_1/p}}{\pi d}\{2E(k, \varphi) - F(k, \varphi)\}, \tag{8}$$

where $\varphi = \sin^{-1}\sqrt{\dfrac{X_1/p}{B + (X_1/p)}}$ and $k = \sqrt{\left(1 + \dfrac{B}{X_1/p}\right)\Big/ 2}$.

Since k cannot be greater than unity, this solution holds only for $X_1/p \geqq B$.

That Eq. (8) satisfies the experimental results in the case of carbon monoxide may be seen from Fig. 3, where n computed from this expression

[1] K. T. Compton, Phys. Rev. 11, p. 196 (1918).
[2] J. S. Townsend, Electricity in Gases, p. 180.
[3] Loeb, loc. cit.

is plotted against the effective values of X_1/p. For this curve a has the value 1.87 $(10)^6$ and B equals .005, when the pressure is in mm Hg. The circles represent the experimental relations between the frequency

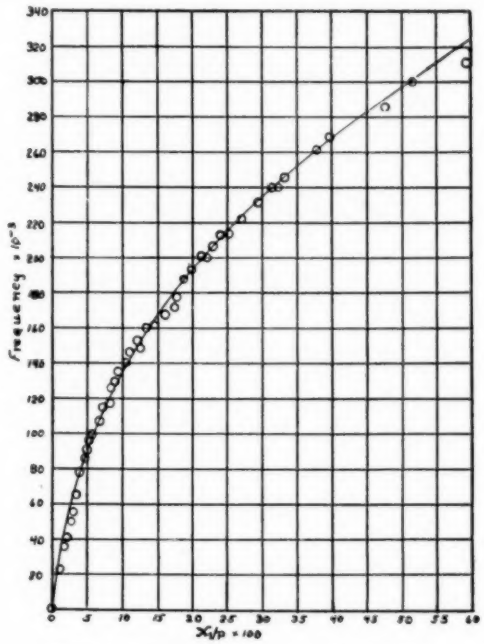

Fig. 3. Frequency as a function of X_1/p

and the effective values of X_1/p determined from the voltage intercepts of the mobility curves. Except for the lowest values the agreement is quite close.

Discussion of Results and Conclusions

The equation for the variation of the mobility of the electrons with field strength and pressure is, therefore, for carbon monoxide,

$$K = \frac{1.87\ (10)^6}{p\sqrt{.005 + (x/p)}}. \tag{9}$$

This equation assumes that the electrons are in a steady state, that is that they have reached their terminal energy of agitation due to the field x. Actually such a steady state was probably never reached in these experiments due to the fact that the field in which the mobility was being measured was continually varying. However, the steady state condition would be approximated very closely if the fraction of the energy (q of Eq. 4) lost at each impact is large. Therefore since the Townsend-Compton equation for the mobility of an electron agrees with

the data of these experiments, it seems reasonable to conclude that the collisions of an electron with the molecules of carbon monoxide are almost completely inelastic. Furthermore, indications are that q is constant; *i.e.*, the fraction of the energy lost at each impact is independent of the energy of the electrons at impact, over the range of energies reached in these experiments.

In the derivation of Eq. (7) from Eq. (6), the mean free path of the electron was assumed to be inversely proportional to the pressure and independent of the velocity of the electron. In general, this is not the case, as has been shown by Townsend,[1] Ramsauer[2] and Mayer.[3] For instance, in the case of nitrogen there is a large increase in the free path for low values of the electronic velocity. Apparently such a change does not exist in the case of carbon monoxide. However if the impacts are nearly inelastic, the energy of the electron would never become very great for the range of pressures and voltages used in these experiments so that a small variation of the free path of an electron with velocity would not be noticeable.

Because of the electronegative character of oxygen it might be expected that carbon monoxide would show a considerable affinity for electrons. The high values obtained for the mobility show that this is not so and that if the electrons unite with the molecules at all they do so very rarely.

UNIVERSITY OF WISCONSIN,
MADISON, WISCONSIN,
November 17, 1922

[1] J. S. Townsend, Phil. Mag. (Dec., 1921).
[2] Carl Ramsauer, Ann. der Phys. **66**, p. 546 (1921).
[3] H. F. Mayer, Ann. der Phys. **64**, p. 451 (1921).

FURTHER EXPERIMENTS ON THE MASS OF THE ELECTRIC CARRIER IN METALS

By Richard C. Tolman, Sebastian Karrer, and Ernest W. Guernsey

Abstract

Inertia of the electric carrier in metals.—Although Tolman and Stewart had apparently demonstrated that the carriers in metals have approximately the same ratios of mass to charge as an electron, it was desirable to verify this result and if possible obtain a more accurate value for m/e by using an entirely different method. An *oscillating apparatus* was constructed, consisting of a copper cylinder $9\frac{1}{8}''$ long, $4''$ outside diameter and $3''$ inside diameter, attached to a brass torsion rod in such a manner that it could be oscillated about its axis with a frequency of about 20 cycles per second. Surrounding this copper cylinder was a coil, containing about 60 miles of No. 38 copper wire, which acted as the secondary of a transformer, and was connected to a vibration galvanometer through a specially designed three-stage amplifier. The tendency of the electrons in the oscillating copper cylinder to lag behind because of their inertia leads to an electromotive force, the effects of which were finally measured by the deflection of the vibration galvanometer, tuned to the frequency of the mechanical oscillations. This galvanometer deflection was then compared with that produced by the known electromotive force accompanying a transverse oscillation of the cylinder across the earth's magnetic field. The apparatus was mounted on a massive concrete pier in a special location 150 yards from the nearest electrical circuits, was constructed without the use of magnetic materials, and was driven by compressed air. The axis of the oscillating cylinder was set parallel to the earth's magnetic field to reduce accidental effects. The apparatus avoids the direct electric connections between moving and stationary parts, and the sudden stopping of a coil of wire, with the attendant chance of buckling and slipping of the wire, which were present in the apparatus used by Tolman and Stewart. The fact that the vibration galvanometer will respond only to the frequency of the desired effect is also important in eliminating accidental effects. *Mass of carrier in copper.* The average of 86 determinations of m/e is 5.2×10^{-8}. However since the means of the first 42 determinations and of the last 44, obtained with the cylinder earthed only through the concrete pier and specially earthed, respectively, are 5.97 and 4.35, and since the corrections for zero amplitude were large, these preliminary results are not regarded as demonstrating a difference between the ratio m/e of the carrier in copper and of an election in free space, 5.66×10^{-8}.

I. Introduction

THE production of an electromotive force by the acceleration of a metallic conductor has apparently been demonstrated by the work of Tolman and Stewart,[1] who measured the pulse of electric current produced by suddenly stopping a coil of wire rotating around its axis.

[1] Tolman and Stewart, Phys. Rev. **8**, 97 (1916); **9**, 164 (1917).

Their experiments showed that this pulse of current was always in the direction which would be predicted on the basis of a mobile *negative* electron for the carrier of electricity in metals, and that the effective mass of this carrier in copper, silver and aluminum was not far different from the mass of a negative electron in free space.

The purpose of the work described in the present article has been twofold. In the first place it seemed desirable to obtain a new demonstration of this production of an electromotive force by the acceleration of a metal, using some method of attack as different as possible from that of Tolman and Stewart, in order to increase our certainty as to the reality of the effect. In the second place it seemed desirable to find a method of measurement which would eliminate certain accidental effects inherent in the earlier procedure and thus make possible a more exact determination of the mass of the carrier in metals. This is a matter of some importance since the earlier work indicated that the mass of a free electron in a metal is somewhat greater than the mass of an electron in vacuo, and if this could be shown to be true it might considerably increase our knowledge as to the inner constitution of metals and perhaps as to the nature of the electron itself.

As will be shown in the sequel, we have apparently again demonstrated the reality of the effect and have developed a method which shows possibilities of considerably greater accuracy than that of Tolman and Stewart. Owing, however, to the resignation of one of the experimenters from the staff of the Fixed Nitrogen Research Laboratory, time was not available to push this new method to such a point as to make certain whether or not the mass of the electron in a metal does differ from its mass in free space. Plans are being made for the continuation of these experiments at the California Institute of Technology where it is hoped this latter point can be definitely settled.

II. Description of Apparatus

In the experiments of Tolman and Stewart, it was felt that irregular accidental electromotive forces were most likely to arise either in the coil itself, because of such mechanical disturbances as slippage or buckling of the wire accompanying the jar of stopping, or at the binding posts for connecting the rotating coil with the twisting wires leading to the galvanometer, because of mechanical strains or temperature fluctuations at these points. For this reason, our new apparatus consisted of a single cylindrical shell of copper which could be oscillated around its axis with a frequency of about twenty cycles per second, and which was surrounded by a coil with many turns of fine wire, connected through an

amplifying set to a vibration galvanometer. The oscillating cylinder thus acted as the primary of a transformer and the coil of fine wire as the secondary. In this way we applied a regular periodic acceleration to a solid shell of metal, instead of applying a sudden change in velocity to a coil of wire, and we furthermore eliminated the necessity of any direct electrical connections between moving and stationary parts of the apparatus.

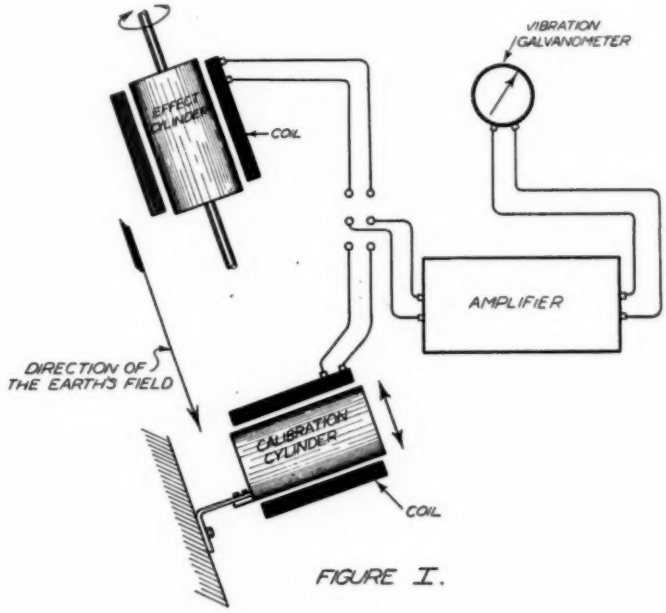

FIGURE I.

The general arrangement of the apparatus is shown schematically in Fig. 1. The potential produced in the secondary by the rotary oscillations of the "effect cylinder" was impressed on a three-stage amplifier, and the amplified current was sent to a vibration galvanometer tuned to the frequency of oscillation.

In order to calibrate the apparatus, a "calibration cylinder" was provided which was made to oscillate at right angles to its axis in such a way as to cut the lines of force of the earth's magnetic field, thus producing a known electromotive force which could be compared with that produced by the effect itself.

Various parts of the apparatus are shown in more detail in Fig. 2. The individual features of the apparatus are described at some length below, in order to make possible an intelligent criticism of the work.

The location.—Preliminary experiments with the apparatus were first carried out in one of the buildings of the Fixed Nitrogen Research

Laboratory. In this first location, however, the continuous accidental variations in electromagnetic conditions were found to be so great as to prevent successful measurement, since the vibration galvanometer was always in violent oscillation when connected through the amplifying set to the coil, even though the coil and cylinder were stationary. A part of this trouble was found to come from electric circuits which were used in the building, some of it, however, apparently came from high potential power lines which entered the Laboratory reservation near the building in question.

The trouble was very greatly decreased by removal to an isolated spot, one hundred and fifty yards from the nearest building with electric circuits, and considerably further from the high potential lines.

The concrete pier.—In order to reduce accidental effects due to motion in the earth's field it was desirable to set the effect cylinder with its axis of oscillation parallel to the earth's magnetic field, and to have the apparatus mounted as solidly as possible. For this purpose we constructed a concrete pier with its northern face approximately parallel to the magnetic dip.

The pier which is shown in Fig. 2 had a total height of about seventeen

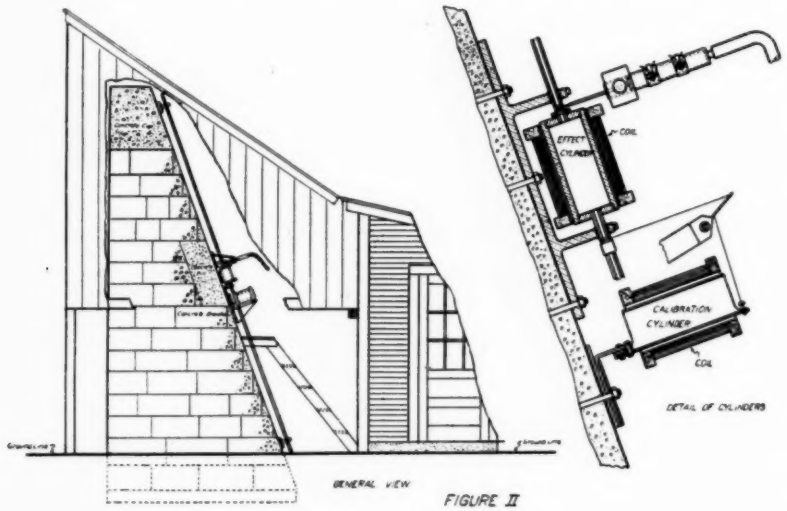

FIGURE II

feet, two feet being below ground. The base of the pier was seven feet from face to back, five feet wide at the face and three feet wide at the back. The cap of the pier was not quite two feet from face to back and three feet wide. It will thus be seen that the structure was quite massive and solid.

The concrete blocks were unfortunately not made from specially

selected materials, but were of course free from iron reinforcement and all the bolts for fastening apparatus to the pier were of brass.

The oscillating system.—The most fundamental part of the apparatus was of course the effect cylinder whose rotary oscillations produced the effect to be studied. This was machined from a copper billet which was cast and then forged at the Washington Navy Yard. The material showed itself in the lathe to be homogeneous and of fine structure due to the forging process. The cylinder was $9\frac{1}{8}$ inches long, with an outside diameter of 4 inches and an inside diameter of 3 inches. The cylinder was provided with copper disks on the two ends as shown in cross section in the detail view in Fig. 2. These disks were $\frac{5}{8}$ inch in thickness and were sweated into place.

These disks formed the means of attachment for the rod the torsion of which provided the restoring force for the rotary oscillations. In order to eliminate magnetic effects due to torsion, this rod was made from special non-magnetic "Navy Brass" such as is used in the construction of torpedoes. The rod was hexagonal in cross section, $\frac{5}{8}$ inch from flat to flat. The distance from end to end between clamps was 14′ 10″, which made the period of oscillation about twenty cycles per second.

This hexagonal rod was provided with brass bushings 25/32″ in diameter on each side of the cylinder, which rested in brass bearings as shown in cross section in the detail, Fig. 2.

Since electrical means for keeping the system in oscillation were obviously ruled out, arrangements were made to drive it by compressed air. The simple air engine used for this purpose, is shown in the detail of Fig. 2, and consisted of a brass cylinder about one inch in inside diameter, provided with a very light brass piston and piston rod which acted on a brass pin set in a copper cross arm fastened across the top of the effect cylinder. The compressed air was admitted to the engine cylinder at the rear end, and this cylinder was slotted from the front end back approximately to the central position of the piston. Under these conditions, somewhat surprisingly, the engine would maintain oscillations without the necessity of any mechanical valves at all, air apparently escaping through the slots in such a way as to make the pressure more effective on the forward than on the back stroke. The front end of the cylinder was surrounded by a housing with a pipe which carried the escaping air away from the slots, thus reducing spurious effects which might arise from the periodic discharge of air in the neighborhood of the coil and incidentally reducing the noise. Compressed air for operating the engine was brought out in storage cylinders, pumped up to 3,000 lb pressure, one cylinder being sufficient for several hours of experimentation.

In addition to the effect cylinder which was oscillated around its axis, a calibration cylinder was provided, as stated above, which was placed with its axis at right angles to the earth's magnetic field and oscillated so as to cut the earth's field in such a way as to produce a reproducible electromotive force which could be compared with the electromotive force arising in the main cylinder from the inertia of the electric carriers.

This calibration cylinder is also shown in some detail in Fig. 2. It was fastened to the concrete pier by a brass bracket which was stiff enough so as to make the natural period of oscillation considerably higher than that of the effect cylinder. It was then driven from the main oscillating system by means of light weight, waxed, silken cords acting on a very light lever as shown in Fig. 2. In this way it was possible to drive the calibration cylinder with the same frequency as the effect cylinder, a matter of great importance since our vibration galvanometer was connected in such a way as to have very sharp tuning. It was shown by actual experiments, using smoked paper and styluses, that the two systems did move with the same frequency.

Two different calibration cylinders were used both made from drawn copper tubing, $3\frac{1}{2}''$ inside diameter and, except for the lips used for attachment of the bracket and cord, the same length as the effect cylinder. One of the calibration cylinders was made with $1/16''$ wall and the other with $1/32''$ wall.

The coils.—The coils which acted as secondaries both in the effect circuit and the calibration circuit were wound from No. 38 enameled copper wire. The windings had an inside diameter of approximately $4\frac{1}{4}''$, outside diameter of $5\frac{3}{4}''$ and a length of $7''$. They contained about 15 lb of wire which gave a length in the neighborhood of 60 miles and a resistance in the neighborhood of 180,000 ohms. The great length of wire was of advantage since the amplifier acted more as a potential detector than as a current detector.

One of these coils was placed around the effect cylinder and fastened as solidly as possible to the concrete pier, to avoid vibration in the earth's field, which would of course have produced accidental electromotive forces. Special experiments were made which led us to the belief that the coil as finally fastened did not have serious accidental electromotive forces from this source. The other coil was placed around the calibration cylinder. The two coils were distinguished as coil No. I. and coil No. II. and were interchanged from time to time. They were found to be so nearly of the same effectiveness that, taking other uncertainties into consideration, no allowance has been made in the calculations for a difference between these coils.

The amplifier.—Connection from the coils was made, through a double throw switch set in paraffin, to a specially designed amplifying set. This amplifying set is shown diagrammatically in Fig. 3. Since the frequency

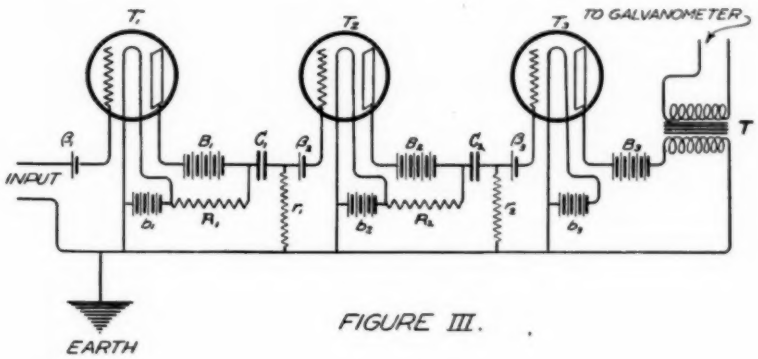

FIGURE III.

of the impressed electromotive force was low, resistance coupling instead of transformer coupling was used between the stages.

Tubes T_1 and T_2 for the first and second stages were furnished us by the courtesy of the Western Electric Co. They each had a voltage amplification constant of about thirty, and were operated with a filament heating current of 0.8 ampere. The first tube T_1 was specially selected as free from "noises." Tube T_3 for the last stage was a regular VT_1, U. S. Signal Corps tube, and was operated with a heating current of 1.1 amperes.

The batteries b_1, b_2, and b_3 for the filament heating currents were Edison six-volt storage batteries. The batteries B_1, B_2, and B_3 for the plate circuits were made from "flash light" cells, B_1 and B_2 giving approximately 140 volts, and B_3 60 volts. The grids were set approximately $1\frac{1}{2}$ volts negative with respect to the filaments by small dry cells β_1, β_2, and β_3.

The resistances R_1 and R_2 for the resistance coupling were Lavite resistances of 200,000 ohms each. The grid leaks r_1 and r_2 were $2\frac{1}{2}$ megohms. The condensers C_1 and C_2 had capacities of 0.5 microfarad each. The primary of the transformer T had an impedance of about 20,000 ohms (25~) and the secondary which was connected direct to the vibration galvanometer had an impedance of about 2,400 ohms (25~).

The vibration galvanometer.—The galvanometer was a Leeds and Northrup vibration galvanometer, provided with a specially light suspension so as to reduce the frequency to the desired value. It had a concave mirror which was illuminated by a single filament lamp, the distance from mirror to ground glass scale being 10′ 1″. The resistance of the galvanometer was 765 ohms, its impedance unknown.

III. Theory of the Experiment

The experiments consisted in measuring as nearly simultaneously as possible the amplitude of the rotary oscillation of the effect cylinder, the amplitude of the transverse oscillation across the earth's field of the calibration cylinder, and the two corresponding galvanometer deflections. These measurements were then followed by a "master" calibration in which the deflections produced by oscillating the effect cylinder itself transverse to the earth's field were compared with the deflections produced by oscillating the calibration cylinder transverse to the earth's field. Hence the experiment as a whole may be looked upon as a comparison of the electromotive forces produced in the effect cylinder itself by the two types of oscillation, rotary oscillation around the axis, and transverse oscillation perpendicular to the axis in such a way as to cut the earth's magnetic field. We may now proceed to an elementary theory of the experiment.

If a longitudinal acceleration a is applied to a metallic conductor, the electrons within the conductor will tend to move relative to the main body of the metal as though the conductor were stationary and the electrons were acted on by the force

$$f = ma, \tag{1}$$

where m may be called the "effective mass" of the electron. On the other hand, if an electromotive force E is applied to a stationary metallic conductor of length l and uniform cross section, the electrons within the conductor will be acted on by the force

$$f = (E/l)e, \tag{2}$$

where e is the charge of one electron. Since the "fictitious" force given by Eq. (1) and the "real" force given by Eq. (2) both tend to make the electrons move relative to the main body of the metal, it is evident that they may be equated in order to get an expression for the electromotive force produced by the longitudinal acceleration of a metallic conductor. We obtain, for the electromotive force E, produced in a metallic conductor of length l, by an acceleration a the expression

$$E = (m/e)la. \tag{3}$$

Let us now consider the rotary oscillations of the effect cylinder around its axis. At any radius r we may evidently write for the instantaneous acceleration the expression

$$a = 4\pi^2\nu^2\theta_e r \sin 2\pi\nu t, \tag{4}$$

where ν is the frequency of harmonic oscillation and θ_e is half the angular

amplitude of oscillation. Substituting in Eq. (3) and taking the length of the conductor at the radius in question as $2\pi r$, we obtain

$$E_e = 8\pi^3\nu^2r^2(m/e)\theta_e \sin 2\pi\nu t \tag{5}$$

as an expression for the electromotive force around a current sheet located in the cylinder at the radius r.

Let us now compare this electromotive force with the electromotive force produced by the transverse oscillation of the cylinder in the earth's field used in calibrating. If θ_c is the half angular amplitude of transverse oscillation, we may write for the maximum flux through a current sheet of radius r, the expression

$$\phi_{max} = \pi r^2 H \sin \theta_c = \pi r^2 H\theta_c \text{ (for small amplitudes)}, \tag{6}$$

where H is total intensity of the earth's field; hence for harmonic oscillations of frequency ν, the electromotive force produced in carrying out the calibration is

$$E_c = 2\pi^2\nu r^2 H\theta_c \sin 2\pi\nu t. \tag{7}$$

Dividing Eq. (5) by (7), we obtain for the ratio of the two electromotive forces

$$\frac{E_e}{E_c} = \frac{4\pi\nu}{H}\frac{m}{e}\frac{\theta_e}{\theta_c}, \tag{8}$$

or solving for the thing of interest, namely the ratio of the effective mass of the electron to its charge, we obtain

$$\frac{m}{e} = \frac{H}{4\pi\nu}\frac{E_e}{E_c}\frac{\theta_c}{\theta_e}. \tag{9}$$

This is the equation which we shall use in calculating our experimental results. It will be noted that the radius r of the particular current sheet has dropped out so that E_e/E_c may be taken as the ratio of the total electromotive forces produced by the rotary oscillation and transverse oscillation of the effect cylinder.

IV. The Experimental Results

The master calibration.—In carrying out the actual experiments, a comparison was made of the galvanometer deflections produced by the rotary oscillation of the effect cylinder and the transverse oscillation of a much thinner walled calibration cylinder. For this reason, in order to use Eq. (9), it was necessary to carry out a master calibration comparing the electromotive forces produced by the transverse oscillation of the effect cylinder and the calibration cylinder.

To do this, at the completion of the regular runs, the torsion rod was cut off short on both sides of the effect cylinder, and one end clamped to the north face of the pier, so that the cylinder was perpendicular to the earth's magnetic field and had a natural period of vibration the same as that of its rotary oscillations. Arrangements were made to drive the cylinder with the same air engine used for producing rotary oscillations, and connections were made with a light silk cord to drive the calibration cylinder. The amplitudes of oscillation were measured with the help of mirrors fastened to the cylinders so as to reflect the image of an electric light filament on to a screen.

The results for both the 1/16″ and the 1/32″ cylinder are given below. Readings of the galvanometer deflection from the effect cylinder and from the calibration cylinder were made alternately, no readjustment of the filament heating currents in the amplifier being made between a given pair of readings. The filament heating current in the last stage was set considerably lower than usual in order to keep the deflection on the scale.

Effect Cylinder, Coil No. II Distance Mirror to Scale 137.5 Inches			1/16″ Calibration Cylinder, Coil No. I Distance Mirror to Scale 130.5 Inches		
Galvanometer Deflection mm	Amplitude of Oscillation mm	Ratio of Deflection to Amplitude	Galvanometer Deflection mm	Amplitude of Oscillation mm	Ratio of Deflection to Amplitude
215	34.8	6.18	38	25.5	1.490
203	31.8	6.38	49.5	33.5	1.477
240	39.3	6.11	44.5	30.5	1.459
226	34.8	6.495	42.5	27.5	1.545
207	30.8	6.72	39	24.0	1.625
		31.885			7.596

Hence the ratio of the deflection produced by the effect cylinder to that produced by the same oscillation of the 1/16″ calibration cylinder is $R = (31.885/7.596)(137.5/130.5) = 4.422$.

The corresponding ratio in the case of the 1/32″ calibration cylinder came out 7.86.

For the same amplitude of oscillation and hence for the same electromotive force applied to each of the primaries, the conductances of the three primaries stood in the ratio 1 to 2 to 16 while the galvanometer deflections were in the ratio 1 to 1.78 to 7.86. These figures show that the transformer system did not act as a pure potential device, but that there was a dissipation of energy in the secondary circuit, which may have been partly due to poor insulation in the secondary coils.

The regular runs.—In our discussion of the theory of the experiment, we derived the following equation:

$$\frac{m}{e} = \frac{H}{4\pi\nu}\frac{E_e}{E_c}\frac{\theta_c}{\theta_e}, \tag{9}$$

connecting the value of the desired ratio of mass to charge of the electron, with experimentally determinable quantities.

For H, the intensity of the earth's magnetic fields, we shall substitute the value 0.57963 gauss which was kindly determined for us by the U. S. Coast and Geodetic Survey with an instrument mounted on the pier near the location of the cylinders. (The value of H a few rods south of the pier was found to be 0.57634.)

The value of the frequency ν was found by attaching a stylus to the torsion rod so that it would mark on a strip of smoked paper drawn past it, a pendulum being also arranged to send a spark, at known intervals, from the stylus through the paper. The value of ν determined in this way was 18.9 per second.

The value of E_e/E_c, the ratio of the electromotive forces produced by the rotary oscillation and transverse oscillation of the effect cylinder, will be taken as G_e/G_cR, where G_e and G_c are the galvanometer deflections from the effect cylinder and the calibration cylinder and R is the ratio determined for these cylinders by the master calibration.

The value of θ_e, the half amplitude of oscillation of the effect cylinder, was read directly in degrees on a scale placed concentric with the rotating cylinder. The value of θ_c, the half amplitude of oscillation of the calibration cylinder, was determined by measuring the amplitude of oscillation of a ray of light from a mirror fastened so as to rock with the calibration cylinder. The value of θ_c in degrees will be taken as $57.30\ d/4l$; where d is the total width of the image on the screen during oscillation, corrected for the original width when stationary, and l is the distance from the mirror to scale.

Substituting the above values into Eq. (9) we obtain

$$\begin{aligned}&\text{For the } 1/16'' \text{ calibration cylinder: } m/e = 7.907 \times 10^{-3}(G_e d/G_c\theta_e l).\\ &\text{For the } 1/32'' \text{ calibration cylinder: } m/e = 4.448 \times 10^{-3}(G_e d/G_c\theta_e l).\end{aligned} \tag{10}$$

In carrying out the actual measurements, one observer controlled the operation of the air engine and read the amplitude of oscillation of the effect cylinder, a second observer inside the darkened observation house observed the amplitude of the beam of light reflected from the mirror on the calibration cylinder, and a third observer adjusted the filament heating currents, read the galvanometer deflections, and recorded the results.

The endeavor was made to obtain simultaneous readings of galvanometer deflection and amplitude of oscillation, and heating currents were not readjusted in the interval between a reading on the effect cylinder and the corresponding reading on the calibration cylinder. Eighty-six measurements were made in all in groups of six or seven. In the first fifty-six measurements, the readings were made in the order: effect, calibration, effect, calibration, etc. In the remaining thirty measurements, they were made in the superior order: effect, calibration, calibration, effect, effect, calibration, etc.

Owing to accidental electromagnetic disturbances, the galvanometer was always in oscillation when connected through the amplifier with one of the coils. This accidental effect was somewhat decreased by specially earthing the cylinders through a wire connected with the earthing wire from the amplifier, instead of relying merely on the connection through the concrete pier. In the first forty-four measurements the cylinders were not earthed, in the remaining forty-two they were earthed. For each group of measurements, readings were made of this accidental effect when the cylinders were not oscillating in order that a correction might be made for it. In the absence of detailed knowledge as to the nature of this accidental effect, the correction was made by simply subtracting from the total galvanometer deflection observed while the cylinder was oscillating, the galvanometer deflection when the cylinder was stationary.

Experimental values for a typical run.—In order to give an idea of the nature of the experimental results, the values obtained in the second group of six measurements are given below as fairly typical.

August 17, 1922, 10:55 A.M.
Distance from mirror to scale, l = 3,468 mm.
Effect Coil No. II., Calibration Coil No. I., 1/16″ Calibration Cylinder.

θ_e (deg.)	G_e (mm)	d (mm)	G_c (mm)	$m/e \times 10^8$
0	9.5	0	7	——
17	23	4.0	180	4.19
21	33	5.1	212	6.35
22.5	40	5.3	260	6.48
24	38	5.8	267	6.03
29	49	6.3	285	7.04
12	16	2.3	127	2.37

The values of m/e in the last column of the above table were calculated from Eq. (10). Before making the calculations, the galvanometer deflections were corrected by subtracting the deflection for zero amplitude.

Average value of mass divided by charge.—The average value of m/e

for the eighty-six measurements was 5.18×10^{-8}, with an average deviation of 1.33×10^{-8}. The average deviation divided by the square root of the number of observations was 0.14×10^{-8}.

V. Critique of the Experimental Work

In order to estimate the value of the results obtained above and in order to plan for more accurate work in the future some consideration of the various possible sources of error will not be out of place.

Effect of accidental oscillation transverse to the earth's field.—Limitations of time made it impossible for us to arrange a satisfactory neutralization of the earth's magnetic field in the space surrounding the effect cylinder. This made it necessary for us to consider the electromotive forces which might be produced by accidental transverse oscillations of the cylinder in this field.

In order to make the effect of such oscillations as small as possible we attempted to make the axis of the effect cylinder as nearly parallel to the direction of the earth's magnetic field as possible. However, since the declination may easily change by 30 minutes between ten o'clock in the morning and four o'clock in the afternoon, no exact parallelism was possible.

To investigate the actual magnitude of the accidental effects which might have been produced, we carried out a special test at the close of our experiments. After the torsion rod had been cut off short on both sides of the effect cylinder, one end of the torsion rod was clamped to the north face of the pier so that the effect cylinder was parallel to its running alignment and so that the cylinder would oscillate transversely with the same frequency as was used in the regular runs. With a total oscillation of about 0.002 radian, we obtained a galvanometer deflection of 54 mm with the galvanometer at its best tuning and the filament currents as usual. This deflection was thus of the same order of magnitude as the galvanometer deflections which were measured in the regular experiments. Since 0.002 radian would correspond to the large motion of 0.01″ in each bearing and since it is improbable that accidental transverse oscillations would consist of a single component having the same frequency as the rotary oscillation, we are inclined to believe that the accidental effect in question was considerably smaller than the main effect. It must be admitted, however, that this accidental effect might have had a serious influence on our results.

Attempts were also made to carry out the experiments with the earth's field neutralized. In the time available, however, we were unable to arrange to reduce the total intensity of the earth's field without at the

same time introducing lack of homogeneity, and under these conditions we apparently got very erratic electromotive forces due to eddy currents in the oscillating cylinder.

Effect of centrifugal action.—Another source of error which must be investigated lies in the action of centrifugal force in making the effect cylinder alternately larger and smaller, and thus changing the flux through the cylinder. Taking account of the density and elastic modulus of copper, it can be calculated that the electromotive force produced in this way would be about 6 per cent of the electromotive force due to the effect. This accidental electromotive force, however, has twice the frequency of the electromotive force due to the effect and hence can be entirely neglected since we showed by special experiments that the vibration galvanometer had no appreciable sensitivity at frequencies other than those for which it was tuned.

Effect of motion of coil.—Any oscillation of the large coil surrounding the effect cylinder would of course have been very serious. After experimenting with various ways of fastening the coil in position, we came to the conclusion that our final strapping of the coil to the concrete pier as firmly as possible had eliminated serious effects of the kind in question.

Correction for zero effect.—Probably the most serious errors in the experiment were due to the large deflection of the galvanometer even when the apparatus was stationary. This zero deflection was usually about 9 to 10 mm when the cylinder was not specially earthed and 4 to 5 mm when the cylinder was connected to the earthing wire from the amplifier. Since the total deflections obtained from the effect were, after correction, usually of the order of 20 to 30 mm, it is evident that the zero effect is very serious.

The correction was arbitrarily made by subtracting the zero deflection from the total deflection obtained while running. Further study of the nature of the accidental forces which lead to the zero effect would be necessary in order to justify such a method of correction. Such a further study could perhaps be made by some oscillographic method. It is interesting to note that the zero effect could not be greatly reduced either by "tuning" out or by connecting a compensating coil so as to "buck" the effect coil. Electrostatic shielding might be helpful.

Evidence that the method of correcting for the zero deflection was not entirely correct is shown by the fact that the average value of m/e for forty-four runs in which the cylinders were not specially earthed was 5.97×10^{-8} while it was 4.35×10^{-8} for the forty-two runs in which the zero effect had been decreased by the special earthing.

VI. Discussion and Conclusion

It is felt that the work presented above may be regarded as another fairly satisfactory demonstration of the production of electromotive forces by the acceleration of a metallic conductor and as indicating again that the mass of the carrier in metals is about the same as the mass of an electron in free space. The new work taken by itself alone is perhaps not as convincing as the work of Tolman and Stewart, because of the greater complexity of the apparatus, because of the fact that time did not permit a satisfactory neutralization of the earth's field, and because further developments of the method would be necessary in order to show that the direction of the effect is that predicted on the basis of a mobile *negative* carrier. Our total certainty as to the reality of the effect is, however, greatly increased by the fact that two such widely divergent methods have led to concordant results.

Values of m/e obtained in different ways are given below, in grams per abcoulomb.

m/e in free space 5.66×10^{-8} (cathode rays)
m/e in copper 6.24×10^{-8} (Tolman and Stewart)
m/e in silver 6.73×10^{-8} (Tolman and Stewart)
m/e in aluminum 6.50×10^{-8} (Tolman and Stewart)
m/e in copper 5.18×10^{-8} (Tolman, Karrer and Guernsey).

It is evident that our data are not yet accurate enough to determine whether the mass of the electron in a metal is precisely the same as that in free space or not.

The work described above was made possible partly by a grant from the American Association for the Advancement of Science, partly by help from a private source, but largely by the support of the Fixed Nitrogen Research Laboratory of the U. S. Department of Agriculture. The authors desire to express their thanks to these various sources of support, and in particular to express to the Government their appreciation of the policy of encouraging the staff of a government laboratory to devote a portion of their time and facilities to the investigation of fundamental scientific questions which have no immediate bearing on the main problem of the laboratory. It is believed that such a liberal policy is of great importance in maintaining a proper scientific attitude on the part of the staff of a research laboratory.

Fixed Nitrogen Research Laboratory,
Washington, D. C.,
December 5, 1922

THE ELECTRICAL CONDUCTIVITY OF MOLYBDENITE

By A. T. Waterman

Abstract

Electrical conductivity of molybdenite (MoS_2) as a function of voltage and temperature.—Measurements of the currents through narrow flat strips cut perpendicular to the crystallographic c-axis gave results for the range from 0° to about 200° C, in agreement with the equation: $i = KV^b e^{-k/T}$, where, for the mineral in the ordinary state, k is about 3,000 and b generally about 1.6. When the voltage is increased to a critical value, breakdown occurs, due to the electric heating. An expression is derived for the breakdown temperature, which is shown to increase as k diminishes. Above 200° irregularities appear; and after heating to 400° and higher or after current heating beyond the breakdown point, the conductivity at ordinary temperatures is usually permanently improved, and k is decreased. In fact, by the use of proper current cycles, a strip may be transformed by stages from a very poor conductor (resistance several megohms) into a reasonably good conductor (resistance only a few ohms), obeying Ohm's law ($b = 1$). At the same time, k diminishes and the breakdown temperature rises until the break disappears at the limiting value of k predicted by the equation; also the *photoelectric sensitivity and dielectric polarization* disappear. A high potential discharge likewise increases the conductivity. This remarkable *permanent change of conducting state* may indicate a corresponding change of structure from an α to a β form, as suggested for selenium. If the constant k is interpreted as being equal to φ/R, where φ is the energy required to change a bound to a free electron and R is the gas constant, then φ is computed to vary from 0.26 volt for MoS_2 in its normal state to 0.13 for the conducting state. This may be of interest in connection with the electron theory of conductivity.

THE mineral molybdenite (MoS_2) is one of an interesting class of substances, the poor conductors of electricity, and has been the subject of considerable research, chiefly in regard to its optical properties and its photoelectric sensitivity.[1] The writer was led to the present investigation by peculiarities noted in its conductivity when examining its thermionic emission.[2] The general behavior of a fresh sample of molybdenite when heated by an electric current resembles that of any material having a large negative coefficient of resistance, including breakdown, and is shown graphically in the above-mentioned paper by the author.

Inasmuch as Ohm's law is not obeyed by molybdenite (like many other

[1] Koenigsberger and Schilling, Centralblatt f. Mineralogie, p. 454, 1905; Coblenz, Bureau of Standards, Scientific Papers **15**, 121, 1919; **16**, 595, 1920.

[2] Waterman, Phil. Mag. **33**, 225, 1917.

substances of this class), it has seemed best in this investigation to examine the effects of temperature and applied e.m.f. on the current transmitted rather than on the resistance as ordinarily done. In all experiments the material was used in the form of narrow flat strips of length generally between 1 and 2 cm. The current was passed lengthwise through the strip, at right angles to the crystallographic *c*-axis. The strips were mounted in a number of ways (soldering, copper-plating and soldering, and clamping between leads of different materials), but the method of mounting did not appear to change the essential behavior when due account had been taken of the effect of the mounting process (*e.g.*, heating) on the state of the strip.

Electrical conduction at ordinary temperatures.—By observations on the variation of current with temperature under constant applied potential difference, and on the variation of current with applied e.m.f. at constant temperature, the following formula for the conductivity of molybdenite in its ordinary state was found to hold to a fair degree of approximation:

$$i = KV^b e^{-k/T}, \qquad (1)$$

where i is the current, V the applied e.m.f., T the temperature absolute, and b, k and K are constants. The value of b is generally about

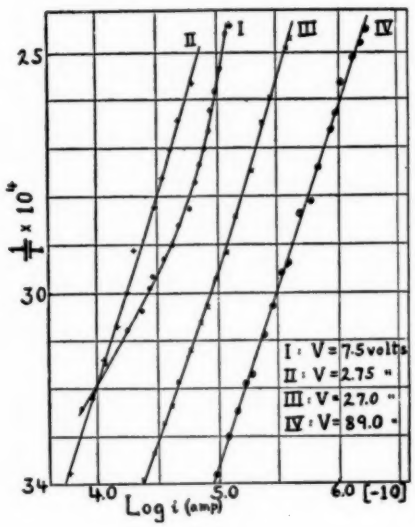

Fig. 1

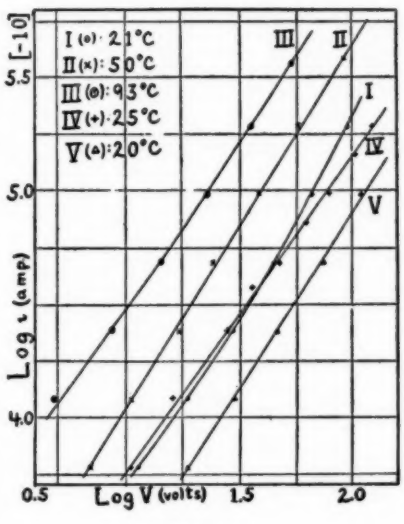

Fig. 2

1.6, although for one strip a value of 2.8 was found. k is nearly always approximately 3,000 degrees. K is a function of the dimensions of the strip, pressure applied at contact, etc. The graphs in Fig. 1,

where the logarithm of the current is plotted against the reciprocal of the absolute temperature, show the degree of verification of the constant e.m.f. relation for four values of the latter, from 2.75 to 89.0 volts. Graph I. shows a slight fatigue effect common to fresh strips, which causes a departure from the linear relation. The temperature range employed was from 0° C to 150° C, obtained in an oil bath. Attempts to secure greater range by means of an electric oven led to inconsistent and uncertain readings above about 200° C, due apparently to partial breakdown which is facilitated by rise in temperature of the surroundings. The graphs in Fig. 2, where the current is plotted logarithmically against the applied e.m.f., show the results of the observations at constant temperature, maintained by an oil bath.

Change in conductivity after treatment at higher temperatures.—Assuming the validity of the Eq. (1), a linear relation should be found between log V and $1/T$ at constant current. The extent of the agreement is shown in Fig. 3 where a number of curves are given for successively

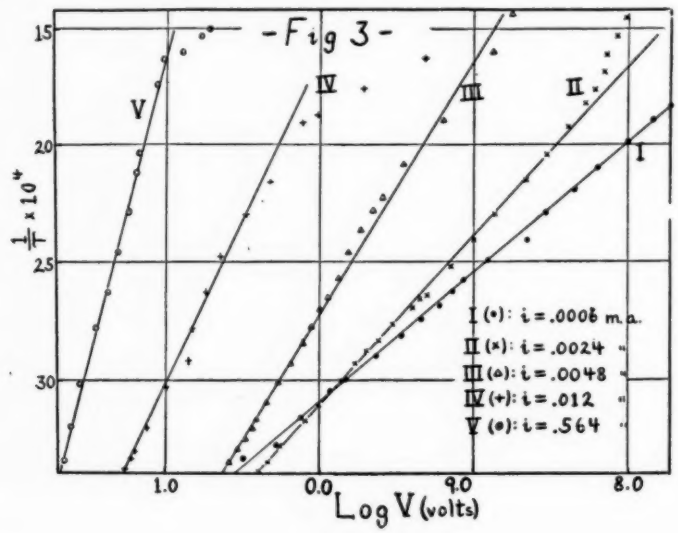

Fig. 3

larger values of the (constant) current, from observations made in the oven from room temperature up to 400° C and higher. The oven method of heating proved here more satisfactory due to the decrease in the applied e.m.f. as the temperature was raised. Heating in the oil bath gave results consistent with the formula for $k = 3{,}000$ and $b = 1.5$ to 1.6. From Fig. 3 it appears that the type of formula found above is satisfied for temperatures at least below 200° C. At some point above this tempera-

ture each curve departs from the linear relation, in many cases showing irregularities of which some were traced to contact variations. But the outstanding feature of these results is that the slope of the curve, which is proportional to b/k, increases with each series of observations. The ratio b/k is not however a function of the current, since, when the heating is carried to high temperatures, the cooling curve (not shown) for any particular value of the current has a greater slope than the heating curve but the same slope as the heating curve for any other current to which the strip is then subjected. Thus the passage of the current through the strip at temperatures over 200° C seems to result in a permanent increase in the ratio b/k, while for temperatures below this point b/k remains substantially constant. The value of b was found to be a maximum for new strips, consequently this permanent increase in b/k must be attributed to a marked decrease in the value of k. The constant K also undergoes considerable change but as it is quite sensitive to contact variations little may be concluded from these changes.

The phenomenon of breakdown.—The break is encountered only when the strip is heated by means of the current. Unless suitable resistance is provided in series, there is a large discontinuity in both current and voltage at the break, the current rising to many times its former value with a corresponding drop in the voltage. With proper precautions however the break may be made to take place slowly and continuously and the current and voltage are comparatively stable. As the current is made to increase continuously, the potential difference across the strip at first increases, reaching a definite critical maximum (the break), and then decreases steadily. This phenomenon has been explained by Lyle [1] in the case of boron. The explanation is based upon the fact that the condition for stability for any reading is that of equilibrium between the rate of heating by the electrical power and the rate of cooling by radiation, conduction, etc. If the material has a large enough negative coefficient of resistance, the heating effect may automatically increase more rapidly than the cooling effect. Thus there comes a point where there can be no equilibrium between the two unless either the temperature rises to a high value or the rate of increase in electric power is limited by external resistance. Since the rate of heating may be taken to be the product of the current and the voltage and the rate of cooling for a given set-up equal to $c(T - T_0)^x$, where $T - T_0$ is the difference in temperature between the strip and its surroundings and c and x are constants, the conditions under which breakdown occurs may then be readily derived from Eq. (1).

[1] Phys. Rev. (2), 11, 253, 1918.

Differentiating (1) logarithmically with respect to i

$$\frac{1}{i} = \frac{b}{V}\frac{dV}{di} + \frac{k}{T^2}\frac{dT}{di}$$

for the range over which k is constant. The condition for the break is $dV/di = 0$. Hence

$$\frac{1}{i} = \frac{k}{T^2}\frac{dT}{di}.$$

But

$$\frac{dT}{di} = \frac{dT}{dP}\cdot\frac{dP}{di},$$

where P is the power supplied, and since V is constant at the break, $dP/di = V$, while dT/dP may be found from the condition for equilibrium $P = c(T - T_0)^x$, *i.e.*, $dT/dP = (T - T_0)/Px$. Hence,

$$\frac{k}{x} = \frac{T^2}{T - T_0}, \tag{2}$$

which gives the temperature of the break for particular values of x, k and T_0.

For a given arrangement of the apparatus it is seen that the temperature required for the break will be higher as k becomes smaller, and consequently more electrical power must be supplied to bring this about. Furthermore, there is a limiting value of k for given value of T_0, the temperature of the surroundings, below which no break will be obtained. In other words, as the value of k diminishes it becomes increasingly difficult to effect a breakdown. The effect of increasing T_0 is to facilitate the break, although it then takes place at higher temperature.

Progressive change in conductivity under current heating.—This behavior is illustrated in Fig. 4, where current-e.m.f. curves are shown for successive current heatings of a single strip in a vacuum. The scale used varies from curve to curve as indicated. A distinct hysteresis effect is apparent, together with permanent increase in conductivity, occurring chiefly when the heating is carried beyond the break. After any single cycle the current-voltage curve is quite reversible for voltages below breakdown.

A fresh strip has a very low conductivity, but after such treatment it appears to possess metallic conductivity at ordinary temperatures since Ohm's law is obeyed, the temperature coefficient of resistance vanishes or even becomes slightly positive, and the specific resistance approaches that of metals. With sufficient heating, however, the hysteresis effect again appears. The resistance of the specimen illustrated was changed

by this process from about 20 megohms for 1 volt at room temperature to 4 ohms. This strip was never brought to a visible red heat and remained unchanged in general appearance.

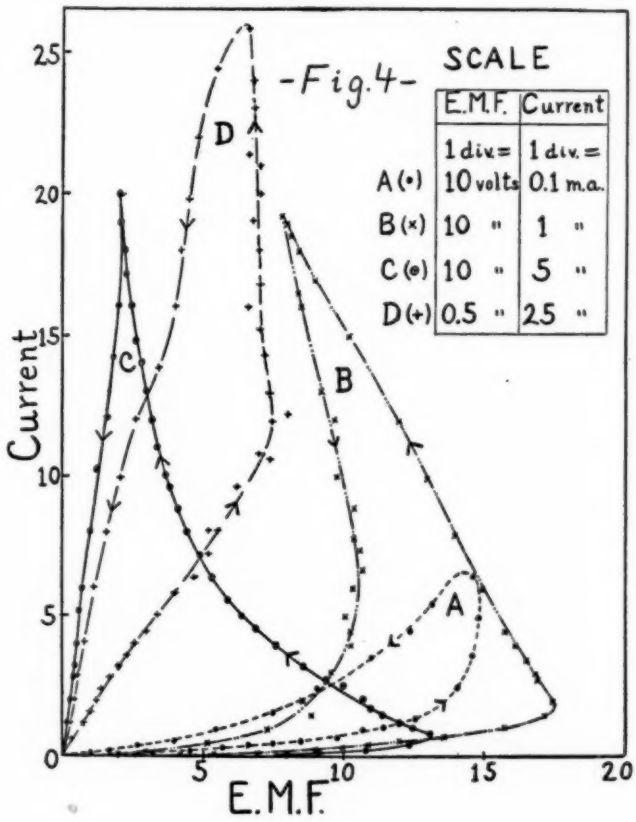

Fig. 4

In two instances a strip in the intermediate state, when brought just to the break, went through a reverse cycle, resulting in permanent *decrease* in conductivity.

Successive breakdown temperatures and values of constants.—Under this treatment the exponent b of the formula decreases to unity (Ohm's law). Its successive values are listed in Table I.

Since the value of k is known at the outset (Graph A), the temperature of the break as calculated from Eq. (1) is $69 \pm 3°$ C. As computed from Eq. (2) the break should occur at $T' = 69 \pm 5°$ C. For the remaining graphs B, C and D the values of k and of T', the temperature of break, may be calculated from the experimental data and Eqs. (1) and (2). These values are shown in Table I., and were checked by calculation based

on the power necessary for breakdown, with the exception of Graph *A* where the applied e.m.f. seems to be the chief factor in the change of state in a manner similar to the initial fatigue effect first mentioned. It will be noted that the value of k decreases from graph to graph as found before, and the temperature of breakdown increases.

TABLE I

Graph	b*	k*	T'	ϕ (equivalent volts)
A	1.65	3,000	69° C	0.26
B	1.65	2,500	82	0.215
C	1.14	2,000	109	0.17
(not shown)	1.0	1,760	138	0.15
D	1.0	1,520	205	0.13

* From heating curve.

As k decreases it is observed that the slope of each successive graph beyond the break increases. From examination of the graphs one might expect to find no voltage maximum for values of k below some limiting value not far below its value 1,520 for Graph *D*. This prediction was verified. Now from Eq. (2) it is seen that under the conditions of this experiment there is no real value of T', *i.e.*, no voltage maximum, when k is less than about 1,450. This fact strengthens the validity of the foregoing discussion.

Interpretation of k.—The relation $i = K_v e^{-k/T}$ is consistent with the expression found by Koenigsberger and Schilling [1] for the temperature variation of specific resistance for a number of poor conductors. In the theory underlying this relation kR is the latent heat (at constant volume per gram electron) of a hypothetical chemical reaction giving rise to free electrons, R being the gas constant. If this significance is attached to k in the present case, the mean energy ϕ thus required to produce a free electron is computed to be 0.26 equivalent volts for molybdenite in its normal state. This does not appear to be an impossible value, being considerably less than the corresponding quantity for thermionic electron emission (or, more briefly, "thermelectron" emission), for photoelectrons, and for electrons produced in ionization of gases. Furthermore, ϕ decreases as metallic conduction is approached, as might be expected, its values being listed in Table I. for the specimen there considered. This interpretation then yields results which are so far consistent with the ordinary electron theory conception of conduction and insulation. Thus a large value of k would be indicative of an insulator for which a corre-

[1] Koenigsberger and Schilling, Ann. der Phys. **32**, 179, 1910.

spondingly large e.m.f. would be required to effect breakdown, though this would be expected to occur under less electrical power and with very slight rise in temperature above the surroundings. A small value of ϕ, on the other hand, would mean metallic conduction and absence of breakdown. An equilibrium theory of electrical conduction has been developed by the writer along these lines, and will shortly be published.

Miscellaneous observations.—(1) The light sensitivity in conduction of a fresh strip of molybdenite becomes inappreciable as metallic conduction is approached.

(2) The unipolarity of a fresh sample is in general slight.[1] However, a moderate e.m.f. applied in one direction may cause a temporary decrease in resistance (to $\frac{3}{4}$ or $\frac{1}{2}$ its original value) to a small current passed in the opposite direction, but the effect soon disappears. The effect was not cumulative either in magnitude or duration; hence some variety of electrolysis seems out of the question, and a Peltier effect inadequate. This effect disappears as metallic conduction is brought about.

(3) Heating to redness in a Bunsen flame for several minutes reduced the resistance to $\frac{1}{2}$ or $\frac{1}{4}$ its value, but further heating produced practically no further effect.

(4) The resistance was diminished to about half value by the momentary passage of a high voltage discharge, as from a small induction coil, but repetition caused no further decrease.

(5) The resistance is not affected by strong magnetic fields.

(6) Slow oxidation occurs on heating in air, the products being given as SO_2 and MoO_3, the latter forming in crystals on the surface of the strip. This does not seem to affect the general behavior of the substance otherwise than would be expected. Under a low power microscope oxidation is seen to be preceded by local eruptions of a dark blue liquid, mentioned by Coblenz [2] and presumably due to a lower oxide of molybdenum.

Discussion of conduction in ordinary state.—In accounting for the initial relation between current and e.m.f. at constant temperature, if the number of conducting electrons is assumed independent of the e.m.f. applied, we have as possibilities:

(1) Variation in contact conditions. This seems unlikely, since the current-voltage function does not appear to be affected by changes in nature or pressure of contact.

(2) Action resembling space charge effect. The form of the function $i \alpha V^{1.6}$ recalls Child's law for thermionic emission, but such an explanation does not seem compatible with the temperature variation. More-

[1] Cf. Coblenz, Bureau of Standards, Scientific Papers **16**, 595, 1920.

[2] Coblenz, Bureau of Standards, Scientific Papers **15**, 155, 1919.

over, the same law should then hold even more for greater concentrations of the free electrons, where Ohm's law holds instead.

(3) E.m.f. of polarization varying in such a way that the resultant electric intensity would produce the observed function. Thus the temporary polarization produced by an applied e.m.f. may be the fatigue effect of a stronger instantaneous polarization.

(4) Orientation of elementary crystals under action of the electric field, thus increasing the mean free path of the conducting electrons. This explanation, commonly reached for similar phenomena by the process of elimination, is hardly open to direct argument at present.

If it be assumed that the number of free electrons is a function of the applied e.m.f., we may imagine a gradual breakdown of the material as a dielectric or possibly ionization by collision if the mean free path is as long as the recent experiments of Bridgman indicate for metals, since an electronic kinetic energy approaching 0.26 equivalent volt might not then seem impossible. As evidence may be mentioned the effect of a high potential discharge on the state of a fresh specimen and the similar change illustrated in Graph *A*, Fig. 4, where the heating was slight.

Discussion of permanent change in conductivity.[1]—The remarkable permanent or semi-permanent change in conductivity may be closely bound up with the nature of the temporary change produced by temperature and electric field, in that the latter when carried far enough bring about a different condition for equilibrium within the material. The only evident change in physical properties is an increase in hardness. No chemical or x-ray analyses were made of the substance in its state of metallic conduction. The purity of the mineral renders unlikely any extensive reaction with impurities contained. The most reasonable supposition is suggested by the prevalent view in regard to the constitution of Se, that molybdenum sulphide may exist in two forms, α of high resistance and β of low resistance. By means of various agencies (heat, electric field and light) the ordinary form α may be transformed into the β variety. α would be characterized by a large value of k and β by a small value. It would be further necessary to credit the form β with metallic conductivity, which is possibly an objection to this hypothesis although it may be that a very small value of k in itself necessitates metallic conduction.

One other compound of molybdenum with sulphur is known, namely, MoS_3, and if a chemical change occurs it may be the formation of metallic molybdenum within the substance according to the reaction: $3MoS_2$

[1] At present writing it appears that the condition of improved conductivity is not stable but that the substance tends slowly to revert of itself to its original state.

$\rightarrow 2MoS_3 + Mo$. This might be expected to cause a decrease in the mean value of k, followed by increasing evidence of metallic conduction. A fact of uncertain significance in this connection is the author's discovery [1] of an emission of Mo^{++} ions from molybdenite at temperatures near the change of state.

In explanation of the light sensitivity of molybdenite in its conduction it is suggested that the absorption of radiation would decrease the mean energy necessary to free an electron and thus the resulting decrease in k would show in an increase in current. In connection with the curious light negative response found by Coblenz, [2] the permanent decrease in conductivity found under special conditions is interesting. For the explanation of this effect the hypothesis of the existence of two forms of the crystal appears to be the most illuminating.

This paper comprises the results of experimental investigations begun at the University of Cincinnati and completed at Yale University.

SLOANE PHYSICAL LABORATORY,
YALE UNIVERSITY,
August 25, 1922

[1] Waterman, loc. cit.
[2] Coblenz, Bureau of Standards, Scientific Papers **16**, 595 (1920).

DETERMINATION OF VISCOSITIES AND OF THE STOKES-MILLIKAN LAW CONSTANT BY THE OIL-DROP METHOD

By Yoshio Ishida

Abstract.

Viscosities of nine gases, determined by the oil-drop method.—Millikan determined the value of e, the elementary charge, from measurements of the rate of fall of charged droplets in air, assuming the coefficient of viscosity to be $1{,}823 \times 10^{-7}$. Now that e is known, the method may also be used to determine coefficients of viscosity. Using carefully purified gases, tested spectroscopically and by density measurements, the results of long series of measurements in *argon, helium, hydrogen, methane, ethane, isobutane, nitrous oxide, and carbon dioxide*, when reduced to 23°, come out, respectively, 2,210, 1,981, 880, 1,079, 927, 755, 1,449, and 1,471, each times 10^{-7}. These agree with such other reliable determinations as are available for comparison, and are probably accurate to within 0.3 per cent. Isobutane is the first gas whose viscosity has been measured near its condensation point.

Coefficients of slip and of diffuse reflection for clock oil drops in the above nine gases.—As pointed out by Millikan, from hydrodynamic and kinetic theory, the constant A in the correction term for Stokes' Law, $(1 + Al/a)$, is equal to the coefficient of slip ζ divided by the mean free path l, and also to $0.7004(2 - f)/f$, where f is Maxwell's coefficient of diffuse reflection, hence from measurements of A both may be computed. The values of A for the nine gases were found to vary with the gas from 0.811 for hydrogen to 0.901 for helium, and they give corresponding values of f varying from 0.926 to 0.874. The results for air and CO_2 agree closely with those of Van Dyke.

Determination of the elementary charge by the droplet method.—The measurements in air give, incidentally, $(4.770 \pm .014) \times 10^{-10}$ e.s.u., in good agreement with Millikan's more accurate value, $4.774 \pm .005$.

Introduction.

THE problem of a sphere moving through a viscous medium has received renewed attention in recent years in connection with various physical investigations, *e.g.*, the determination of the elementary charge (electron). Stokes [1] came to the conclusion from hydrodynamical considerations that a sphere of radius a moving at a steady speed v experiences a resisting force F given by

$$F = 6\pi\eta av,$$

η being the viscosity of the medium. Millikan,[2] however, found in

[1] Trans. Camb. Phil. Soc., Vol. IX., p. 8 (1850).

[2] Phys. Rev., XXXII., 1911, p. 366.

carrying out the oil-drop experiment that the formula is not exact if the sphere is so small that its radius is comparable with the mean free path of the molecules of the gaseous medium. A good deal of discussion [1] has centered round the correction necessary to bring Stokes' formula into agreement with experiment, and it is found practicable to denote it, generally, as a dimensionless correction factor, which multiplies the resisting force by $f(l/a)$, where l is the mean free path. Millikan gave to this function the form $(1 + A(l/a))$, and has carried out, with his pupils, a considerable number of experiments to determine whether or not A varies with the nature of the surface [2] and the nature of the gas.[3] The results have been altogether unambiguous in demonstrating such a variation with the nature of the surface. A variation with the nature of the gas was also indicated but with less certainty. At Professor Millikan's suggestion I have carried out with his apparatus the following experiments upon a considerable number of gases, paying especial attention to the monatomic gases helium and argon with which he anticipated the largest divergence from the behavior of ordinary gases.

Method of Calculation.

If a falling oil-drop [4] has a mass m and has reached a terminal velocity v_1, then by Stokes' Law we have

$$mg = 6\pi\eta a v_1.$$

This equation has however to be modified for very small drops by the above factor $f(l/a)$ to represent the various empirical or theoretical corrections advocated and we write

$$mgf\left(\frac{l}{a}\right) = 6\pi\eta a v_1. \tag{1}$$

If now the drop has attached to it an electron (charge e) in an electrostatic field E opposing gravitation and a terminal velocity v_2 is attained we have

$$(Ee - mg)f\left(\frac{l}{a}\right) = 6\pi\eta a v_2. \tag{2}$$

[1] Cunningham, Proc. Ray Soc. (1), 83, p. 357 (1910); Knudsen, Ann. Phys., vol. 36, p. 981 (1911); Arnold, Phil. Mag., XXII., p. 755 (1911); Zerner, Phys. Zeit., XX., p. 546 (1919); Weysenhof, Ann. Phvs., vol. 62, p. 1 (1920).

[2] J. Y. Lee worked with shellac drops, Phys. Rev., Vol. IV., p. 420 (1914); O. Silvey and J. Derieux with Hg drops, Phys. Rev., Vol. VII., p. 87 (1916), Vol. XI., p. 203 (1918).

[3] Hydrogen was used by Millikan, W. H. Barber, and Ishida, Phys. Rev., Vol. V., p. 334 (1915), abstract, and J. Lassalle worked with CO_2 (Phys. Rev. 17, 354, 1921).

[4] The oil used in this work was "Superfine" Clock Oil furnished by the Wm. Nye Co.

Equations (1) and (2) are insufficient to determine the unobserved quantities e and a since $f(l/a)$ is unknown. Following Millikan (loc. cit.), however, we may employ a process of successive approximations depending on the assumption [1] that $f(l/a)$ can be approximately represented by the expression $[1 + A(l/a)]$, *A being the constant which I have called the Stokes-Millikan Law Constant.*

If we write σ for the density of the oil and ρ that of the gas so that allowing for buoyancy

$$m = \frac{4}{3}\pi a^3(\sigma - \rho)$$

and introduce what Millikan calls the "apparent charge" e_1 given by

$$e_1^{2/3} = \left(\frac{4}{3}\pi\right)^{2/3}\left(\frac{9\eta}{2}\right)\frac{v_1^{1/3}(v_1 + v_2)^{2/3}}{E^{2/3}}, \tag{3}$$

then we may formally solve equations (1) and (2) and obtain

$$a^3 = \frac{3Ee}{4\pi(\sigma - \rho)}\frac{v_1}{(v_1 + v_2)}, \tag{4}$$

$$e_1^{2/3} = e^{2/3}\left(1 + A\frac{l}{a}\right). \tag{5}$$

We shall, further, following Millikan, make use of the fact (kinetic theory of gases) that the mean free path l is inversely proportional to the pressure so that

$$\left(1 + A\frac{l}{a}\right) = \left(1 + \frac{b}{pa}\right), \tag{6}$$

where b is a constant connected with A by

$$\frac{b}{p} = Al. \tag{7}$$

Equation (5) then becomes linear in $e_1^{2/3}$ and $1/pa$, viz.:

$$e_1^{2/3} = e^{2/3}\left(1 + \frac{b}{pa}\right), \tag{5'}$$

and we can plot the experimentally determined values of $e_1^{2/3}$ from (3) against the reciprocal of the corresponding products pa in which a is given by (4). This latter step is allowable since, although (4) involves the variable e supposed unknown, this quantity is in fact very closely given by Millikan's published work. The straight line thus obtained

[1] Experiment showed that this first-order correction is insufficient when l/a becomes too large and the deviation, in the case of air, was investigated by Millikan (PHYS. REV., April, 1920 (abstract). In the present instance, however, we shall confine ourselves to the first-order term.

has $e^{2/3}$ for intercept and if this differs from the assumed value (Millikan's) we can resubstitute in (4) and obtain a still closer approximation. The slope of the final line thus obtained is then given by

$$\tan \theta = e^{2/3}b \tag{8}$$

so that b as well as e is now determined.

Now the determination of e_1 from (3) assumes that the viscosity has been previously determined. This was the case for air from which the value of e has hitherto been derived, but when we proceed to other gases, as in the present work, it is found that the values of the viscosities as given by various experimenters differ widely among each other. Accordingly it has been considered advisable to *use the oil-drop method to determine the viscosity indirectly* by assuming that e must be a constant for all gases. On this latter hypothesis all the various $e_1^{2/3}$, $1/pa$ lines must have the same intercept on the vertical axis, viz., $e^{2/3}$ and the procedure adopted was to assume at first that all the gases have the same viscosity given by $\eta = 10^{-4}$ gm/cm sec. This gives a set of lines of various slopes and intercepts as shown in Fig. 1. The ordinates of these lines are then

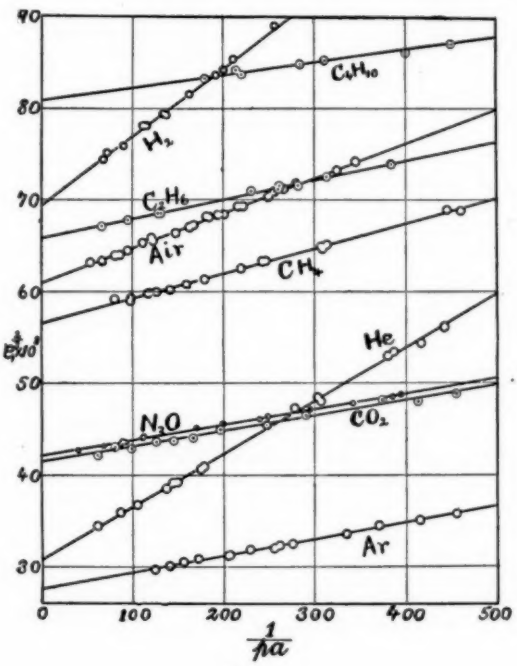

Fig. 1.

multiplied by factors to make them all cut the vertical axis at the same point as shown in Fig. 2, and these factors give the values of the various

viscosities with air taken as standard. The data for these figures are given later.

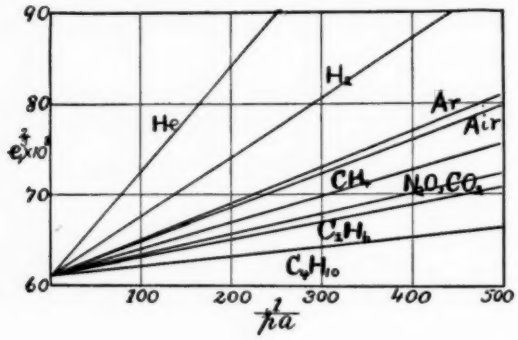

Fig. 2.

From Fig. 2 we may read off the slopes and determine the various values of the constant b by equation (8). The mean free path l is given by Boltzmann's equation [1]

$$l = \frac{\eta}{.3502\rho u\sqrt{\frac{8}{3\pi}}},$$

where

$$u = \sqrt{\frac{3p}{\rho}}.$$

Experimental Arrangement.

The experimental arrangement has been more than once described by Millikan and his pupils and we may refer to an earlier diagram.[2] Two modifications have been introduced: (*a*) all rubber tubing connections have been replaced by glass, and (*b*) in order to avoid contamination of the oil drops by stopcock grease and to prevent the oil in turn rendering the grease unable to maintain a vacuum, the aspirator apparatus shown in Fig. 3 was constructed to replace the corresponding part *A*, *S*, *r* of Millikan's diagram (loc. cit.). Thus the tube *T* is supposed to be continued into the tank. The bulb *A* (100 c.c.) containing the oil which is to be aspirated, and a drop of which is to be suspended between the charged plates, is kept at tank pressure by a communicating tube. The stopcock *S* is carefully ground at one operation into the two sockets *B* and *C*. The part *C* forms the neck of the bulb *D* which completely encloses *B*, the latter being the essential passage for the oil to the aspirator *E*. No grease is used at *B*, the oil itself serving as the seal. Oil leaks

[1] Wiener Sitzungsber., LXXXIV., p. 45 (1881).

[2] Phil. Mag., XXXIV., p. 5 (July, 1917).

through the seal only slowly since by means of the spiral glass tube "shunt" F the interior of D is also at tank pressure. On the other hand, to withstand the possible difference of pressure between tank and atmosphere at C, good stopcock grease is employed, and, as is seen, the oil and grease are kept quite separate. The bulbs G, H, and J serve as "traps" for oil. To form a "cloud" of drops a small amount of oil is first admitted

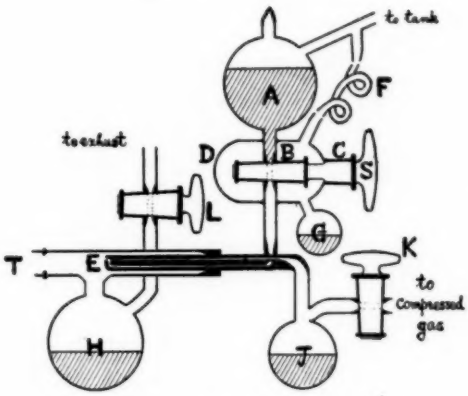

Fig. 3.

into the aspirator nozzle by opening the stopcock S, the oil being driven down by its own weight only. The heat of the hand applied to the bulb J will force any accidental excess out into the trap H. To aspirate, the stopcock K leading to a reservoir of the same gas under pressure is then momentarily opened. Exhaustion [1] of the tank is carried out through the stopcock L and trap H in parallel with the main exhaust so as to ensure that any oil which might come out of the aspirator is drawn into the trap and does not reach the tank. It is important to notice that the glass tubing connections, leading from the apparatus shown to more distant parts, as well as the connections of the main tank system, all contain a considerable length of tubing coiled into spiral form. This supplies that considerable "play" which is often required in adjustments. The completed apparatus was found capable of maintaining a vacuum (the vapor pressure of oil) over several weeks. The tank capacity was about 14 liters.

Preparation of the Gases.

The wide divergence in the viscosity results obtained by different experimenters for various gases has probably been partly due to the difficulty of obtaining very pure samples of gas. It was therefore thought

[1] Diffusion pump assisted by the Gaede mercury pump was used for this work.

necessary to give the greatest possible attention to the elimination of impurities.

Argon.—Pure argon prepared by the calcium arc method,[1] was furnished by the General Electric research laboratory of Schenectady, N. Y., who also supplied a certain amount of 90 per cent pure gas. The tank was washed [2] several times for occluded gases beginning with the cheaper impure gas and finishing with the pure supply. Finally the pure gas was transferred from the reservoir to the tank by means of a Töpler pump through a tube of P_2O_5 and a trap cooled to $-$ 135° C by "pasty" liguorn. The gas in the tube leading from the trap to the tank showed no traces of impurities under spectroscopic test for pressures less than a centimeter or so. Higher pressure showed H_α and Hg lines.

Helium.—The gas, 60 to 80 per cent pure, was supplied from the Texas source. All impurities except hydrogen and neon were easily got rid of by passing through charcoal cooled in liquid air. Liquid hydrogen, which would also have removed these, was not available, but fresh liquid air was used and the diffusion made very slow by passing the gas through 5 meters of small pyrex tubing (2 mm diam.) filled with charcoal grains. The spectrum of the purified helium showed no trace of neon (red line) below a pressure of 4 cms. Further increase of pressure brought out first the H and then Hg lines.

Hydrogen.—Hydrogen was generated electrolytically from platinum electrodes in dilute sulphuric acid, the interior of the generator being water-cooled to diminish the amount of water vapor going over. The gas was cooled with an ice-salt mixture and then passed in succession through P_2O_5, for water vapor, metallic sodium at 100° C for oxygen and cocoanut charcoal cooled in liquid air for other possible impurities such as N_2, CO_2 and the hydrocarbons. This final product was spectroscopically pure.

Nitrous Oxide (N_2O).—Nearly pure (99 per cent) gas was prepared by the White Dental Manufacturing Co., Philadelphia, the impurities being air and CO_2. The CO_2 was removed by bubbling through concentrated KOH solution, and the gas was then passed over P_2O_5 and frozen in a liguorn trap when the residual unfrozen gas (air) was pumped off.

Carbon Dioxide.—This was prepared by heating sodium bicarbonate in a thick-walled pyrex bulb and drying. To remove possible impurities, due to air, the gas was frozen in "pasty" liguorn, the residual gas (air) being pumped off.

Methane.—The gas was prepared by the reaction of methyl iodide on a

[1] Fischer and Ilioici, Ber. Deut. Chem. Ges., 42, p. 527 (1909).

[2] This process is important for all gases including air.

mixture of methyl alcohol and water in which there was a zinc copper couple.

Ethane.—For the preparation of this gas the same scheme as for methane was used, substituting ethyl iodide and ethyl alcohol for the methyl compounds. To generate the gas the mixture was heated to 60° C.

These two hydrocarbons methane and ethane were fractionally distilled by means of liquid air and liguorn paste six to eight times after usual precautions had been taken for CO_2 and water vapor. Otherwise it is very difficult to get rid of the vapor of the iodine compounds. Long trains of zinc had been previously tried without material success.

Isobutane.—Impure gas prepared in the Kent Chemical Laboratory of the University of Chicago and it was only after many fractional distillations that a density of 2.608×10^{-3} was obtained which is near the accepted value.

As a rough check on all these gases except hydrogen and air their densities were fairly carefully determined, and the following table shows the agreement between the accepted values and the present ones after reduction to N. T. P.

	He.	Ar.	CH_4.	CO_2.	N_2O.	C_2H_6.	$_4H_1C_0$(Iso).
Accepted value.....	.179[1]	1.787[1]	.716[3]	1.965[5]	1.966[3]	1.357[7]	2.594[8]
	.178[2]	1.781[2]	.717[4]	1.977[6]	1.978[8]		
Observed value.....	.180	1.780	.719	1.974	1.971	1.363	2.608
		1.784[9]					

Results of Experiments.

During the experiments the temperature was maintained as nearly as possible at 23° C for all gases except air and hydrogen. Temperature corrections for viscosity were made in the case of these two gases by Sutherland's formula, the constants being taken from Landolt and Bernstein's tables. For all other gases the simpler formula

$$\eta = \eta_{23}[1 + .003(t - 23)]$$

was used which is close enough for the small temperature deviations involved.

A summary of the results is shown in Table I. The intercepts and slopes of the lines given in Fig. 1 are contained in the first two columns of the table in the same units as in the diagram. The next column gives

[1] Ramsay and Travers. [2] Watson. [3] Thomson. [4] Baume and Petit.
[5] Raleigh and Leduc. [6] Guye and Pintza. [7] Baume and Parrot. [8] Frankland.
[9] Measured by General Electric Co.

the deduced viscosities, *i.e.*, the multiplying factors for the ordinates of Fig. 1 required to bring all the intercepts into agreement as in Fig. 2 and explained above. These numbers are thus equal to the ratios of the intercept for air to the intercepts for the various gases. The following column gives the constants b which are the slopes of Fig. 2, and are thus equal to the ratios of slope to intercept of the first two columns. The density column is for the actual experimental condition (23° C) and the mean free paths of the succeeding column were calculated from these values (Boltzmann's formula above).

TABLE I.[1]

Gases.	Intercept $\times 10^8$.	$\tan\theta \times 10^3$.	$\eta \times 10^4$.	$b \times 10^4$.	$\rho \times 10^4$.	$l \times 10^5$.	A.	$\zeta \times 10^7$.	f.
C_4H_{10}(Iso)..	80.82 ± .03	14.07 ± .01	.755	1.74	23.9	.275	.834	23.0	.91
C_2H_6.....	65.85 ± .01	20.84 ± .04	.927	3.16	12.5	.466	.891	41.5	.88
N_2O.....	42.13 ± .01	16.92 ± .04	1.449	4.02	18.2	.606	.873	53.0	.89
CO_2.....	41.50 ± .03	16.46 ± .08	1.471	3.97	18.2	.615	.849	52.2	.90
CH_4.....	56.58 ± .02	27.01 ± .05	1.079	4.77	6.6	.749	.838	62.8	.91
Air.....	*61.05* ± .01	*37.66* ± .04	*1.823*	6.17	11.9	.942	.862	81.1	.90
Ar.....	27.62 ± .01	18.09 ± .02	2.210	6.55	16.4	.972	.868	86.1	.88
H_2.....	69.37 ± .01	74.42 ± .12	.880	10.73	.83	1.741	.811	141.2	.92
He.....	30.82 ± .02	57.99 ± .07	1.981	18.82	1.65	2.75	.901	248	.87

The 8th column gives the various values of the constant A as calculated from equation (7).

The data of the various gases from which Fig. 2 is drawn will now be discussed (see Table II.). Measurements for air which, on account of its known viscosity, determine the value of e were repeated at various times throughout the work so as to ensure constancy of working conditions. This part constitutes of course a repetition and verification of Millikan's published work. The values of $e_1^{2/3}$ and $1/pa$ were calculated as explained above from equations (3) and (4), the known value 1.823×10^{-4} for the viscosity of air being used and the value 10^{-4} for all other gases. The corresponding straight lines of Fig. 1 were calculated by least squares.

In the case of air we obtain an intercept of $(61.048 \pm .008) \times 10^{-8}$ as against Millikan's final 1917 intercept of 61.086 and from this on making allowance for the systematic errors[2] which in a larger sense are also probable errors, since they, too, are distributed haphazard, the

[1] The values for the coefficient of slip $\zeta = A/l$ and for the coefficient of diffuse reflection $f = 1.4/(A + 0.7004)$ have been added by the editor for comparison with the results given by Millikan, Van Dyke and others in preceding papers.

[2] Errors of this type will be discussed later.

derived value of the elementary charge is

$$e = (4.770 \pm .014) \times 10^{-10},$$

agreeing with Millikan's value $4.774 \pm .005$ well within the limits of my experimental errors which, as indicated, are somewhat larger than those involved in Millikan's determination.

TABLE II.

	$e_1^{2/3} \times 10^8$.	$1/pa$.	w.		$e_1^{2/3} \times 10^8$.	$1/pa$.	w.
Air Ranges { temp. 22.5 − 26.8° C press. 26.7 − 75.2 cm Hg voltage 3,330 − 5,330 volts	63.20	53.5	2	C_2H_6 Ranges { temp. 23.0 − 23.15° C press. 23.5 − 57.8 cm Hg voltage 1,350 − 4,730 volts	67.62	85.7	1
	63.48	66.5	1		67.75	95.4	2
	63.98	81.0	2		68.52	128.1	2
	64.13	86.4	1		68.57	131.4	2
	64.51	94.7	2		70.85	229.5	2
	65.33	111.2	2		71.18	260.1	1
	65.87	121.0	1		71.37	261.3	1
	65.61	122.5	2		71.55	281.6	1
	66.49	147.0	2		72.50	312.8	1
	67.07	162.1	2		73.82	383.7	1
	67.33	167.3	2		76.41	510.7	1
	68.20	181.4	2		76.98	534.2	2
	68.05	183.9	2				
	68.36	193.4	2	C_4H_{10}(Iso) Ranges { temp. 23.0 − 23.1° C press. 16.7 − 25.2 cm Hg voltage 1,990 − 2,660 volts	83.31	179.5	
	68.42	200.1	2		84.20	214.4	
	69.26	214.6	2		83.77	221.4	
	69.38	221.6	1		84.83	284.2	
	69.93	237.4	2		85.25	310.9	
	70.27	249.2	2		85.76	373.0	
	71.03	256.3	1		87.13	449.5	
	71.13	266.3	2		88.01	520.3	
	71.39	280.4	2		88.81	563.5	
	73.21	324.4	2		89.80	617.2	
	74.52	355.4	2		89.74	642.6	
Ar Ranges { temp. 22.9 − 23.7° C press. 21.0 − 40.0 cm Hg voltage 1,300 − 2,000 volts	29.79	124.1	2	H_2 Ranges { temp. 22.8 − 27.0° C press. 30.7 − 74.7 cm Hg voltage 2,000 − 3,340 volts	74.26	67.9	2
	30.13	139.5	1		75.15	72.4	1
	30.48	153.7	1		75.75	90.1	2
	30.85	172.0	2		78.01	111.5	2
	31.29	204.4	2		78.01	113.8	1
	31.31	206.1	2		78.11	117.5	2
	31.82	227.7	2		79.37	134.1	2
	32.08	255.1	1		79.32	136.9	1
	32.34	261.0	2		81.50	163.2	2
	32.54	274.9	2		83.65	192.4	1
	33.62	333.7	2		84.30	200.5	2
	34.43	369.7	2		84.81	210.9	1
	35.09	414.1	1		88.89	257.0	1
	35.81	455.4	2		96.33	363.2	2

TABLE II. (*Cont.*).

	$e_1^{2/3}\times10^8$.	$1/pa$.	w.		$e_1^{2/3}\times10^8$.	$1/pa$.	w.
CO_2	42.22	63.7		N_2O	42.74	39.9	
Ranges { temp. 22.9 −23.12° C; press. 18.9 −50.2 cm Hg; voltage 1,970 −3,340 volts }	43.09	80.3		Ranges { temp. 22.9−23.15° C; press. 24.7 −71.0 cm Hg; voltage 2,600 −3,980 volts }	43.21	67.7	
	43.40	98.0			43.44	85.9	
	43.27	104.9			43.67	88.4	
	43.73	144.7			43.58	92.2	
	44.04	165.8			44.06	110.5	
	44.92	195.7			44.24	112.8	
	46.56	290.5			45.08	169.9	
	48.17	373.9			45.58	198.8	
	48.03	412.1			46.16	238.4	
	48.82	454.8			46.56	258.9	
	50.86	569.9			47.21	294.9	
	51.57	588.4			47.88	341.4	
					48.51	384.4	
CH_4	59.19	80.0			48.79	393.7	
	59.05	97.5					
Ranges { temp. 22.85−23.13° C; press. 22.6−43.3 cm Hg; voltage 1,940−3,310 volts }	59.26	98.9		He	34.45	61.2	1
	59.60	117.5		Ranges { temp. 22.8−23.2° C (except one 23.9); press. 23.1−67.2 cm Hg; voltage 680 −1,340 volts }	36.46	96.2	2
	59.95	126.3			36.81	104.6	1
	60.23	141.3			38.59	135.6	2
	60.82	158.8			39.18	144.1	2
	61.37	178.5			39.32	148.7	1
	62.52	219.0			40.77	174.8	2
	63.28	242.2			41.05	178.4	1
	63.29	245.5			45.43	247.3	1
	63.59	261.2			47.29	277.4	2
	64.90	306.6			48.43	302.5	1
	64.67	308.4			48.15	307.0	1
	65.08	313.2			53.11	380.6	2
	68.85	445.9			53.48	387.2	2
	68.76	460.9			54.40	416.5	1
	71.70	543.0			56.31	442.3	2
	74.29	665.2					

w is the weight of each obs.
Empty space indicates uniform weight.

The following table gives a comparison of the viscosity values here obtained and those of some other workers for 23° C. The latter were

TABLE III.

$\eta_{23}\times10^7$ ($\eta_{23}\times10^7$ for air taken 1,823).

	He.	H_2.	Ar.	CH_4.	CO_2.	N_2O.	C_2H_6.	C_4H_{10} (Iso).
Other workers' values	2,005[1] 1,988 (1,979)[8] } [2]	890[3] 882[4]	2,258[1] 2,249 (2,238)[9] } [2]	(1,226)[5]	1,471.5[7] 1,500[3] (1,629)[5]	1,488[6]		
Obtained values	1,981	880	2,210	1,079	1,471	1,449	927	755

[1] Schultze. [2] Rankine. [3] Breitenbach. [4] Yen: Phil. Mag., XXXVIII., p. 582 (1919). [5] Grahm. [6] Tisher. [9] Rankine, Proc. Roy. Soc., 83, p. 265, 516 (1910). [7] Van Dyke, Phys. Rev., **21**, 250, 1923. [8] Rankine, Proc. Roy. Soc., 84, p. 181 (1910).

computed from the values at 0° C by means of the Sutherland formula. Those in brackets were computed by a linear formula.

The values here obtained are estimated to be correct within .3 per cent. It will be noticed that in this table most other workers come consistently higher, but this is thought to be due to the fact pointed out before by Millikan that air has generally been given a value about 1.5 per cent too high and other gases have been referred to it. The following table showing the ratios η_{air}/η_{gas} gives excellent agreement whenever these ratios have been accurately determined in preceding work.

TABLE IV.

Values of $\frac{\eta_{gas}}{\eta_{air}}$ *at 23° C.*

	He.	H_2.	Ar.	CH_4.	CO_2.	N_2O.
Other observers	1.082 (Rankine) 1.086 (Schultze for 15°)	.482 (Breitenbach) .484 (Yen)	1.224 (Rankine)	.632 (Graham for 20°)	.808 (Van Dyke) .812 (Breitenbach) .841 (Graham for 20°)	.841 (Graham for 20°)
Our values.....	1.087	.483	1.212	.592	.808	.795

GENERAL ACCURACY.

In view of the fact that the viscosities and other quantities given above were indirectly derived, it is important to form an estimate of their probable errors. In calculating the slopes and intercepts of the lines of Fig. 1, the observational data were divided into two classes. Where the same drop was kept under observation during many consecutive falls through the telescopic field for, say, an hour or so, the result was given double the weight given to periods of half this time or less. There were a few cases that had to be discarded, the results being for some unexplained reasons 10 to 50 per cent out. The probable errors in slope ($e^{2/3}b$) and intercept ($e^{2/3}$) were derived in the usual way[1] and are recorded in Table I.

Besides these "probable" accidental errors there remains the possibility of systematic errors, *i.e.*, errors remaining constant and of one sign throughout the experiments. For experimental reasons, which need not be discussed at present, we know that such systematic errors can only have entered as approximately *constant percentage* errors into the

[1] See, *e.g.*, Johnson's The Theory of Errors and Method of Least Squares, pp. 108.

data for the ordinates and abscissæ of Fig. 1. The results would therefore be a shearing effect on the diagram not affecting the linearity of the observational points. The errors would enter into the ordinates $e_1^{2/3}$ through the factors (equation (3)): distance of fall, time of fall and voltage, and the maximum possible systematic error is estimated at .3 per cent. Since the viscosities are essentially ratios of ordinates (intercepts) they are independent of this possible error provided the experimental conditions are identical.

When looked at from the practical point of view of agreement with other dependable determinations, the intercepts, *i.e.*, the viscosities, entirely justify the estimate of an uncertainty not greater than about 0.3 per cent. For the viscosities of H_2 and CO_2 have recently been determined with an accuracy of about 0.1 per cent by Yen and Van Dyke by the constant deflection method—a method far transcending in accuracy those previously used—and the present determinations are seen from Table III. to show no deviation from their values greater than a fourth of a per cent. Further the ratio of the viscosities of helium and hydrogen with respect to air have been previously accurately determined and Table IV. shows that these ratios also are practically identical with those here found. The divergence of the present determinations of the viscosities of CH_4 and N_2O from Graham's values is without significance in view of the early date of Graham's work.

It is worthy of remark that the method here used, unlike the usual methods, is just as applicable to vapors near their condensation points as to permanent gases, and that *the viscosity of one such vapor C_4H_{10} has for the first time been accurately determined.*

I estimate the practical uncertainties in the slopes, however, *i.e.*, in the values of A as very much greater than the uncertainties in the viscosities. Indeed Millikan estimates that when his value of e (intercept) is determined with an uncertainty of not more than 0.1 per cent his slope may be in error by as much as 1 per cent. In this work, in which smaller numbers of drops in a given gas were taken, the uncertainty in A may well in some cases be as much as 2 per cent. Nevertheless the excellent agreement between my values of A in both air and hydrogen with the values taken some years earlier by Millikan in the same gases, viz., .861 in air against his .864 and .811 in H_2 against his .815, speaks well for the duplicability of results by different observers under different conditions. It is not so satisfactory to compare my value of A for CO_2, viz., .849 with that obtained by Lassalle, viz., .825, but the slope for CO_2 is the least reliable of any for the observations were made rather hurriedly.

Nevertheless no consideration of experimental errors appears to be

able to account for the variations in A found in Table I. where the lowest value (hydrogen) is .811 and the highest (helium) .901.

I look upon this data then as furnishing good evidence that the A in the Stokes-Millikan formula varies with the nature of the surrounding gas. It is interesting that the monatomic gases He and Ar both show very high values of A, but the variation of A with the nature of the gas is apparently not large enough in comparison with the precision of my results to bring to light the exact law of dependence of A upon other molecular characteristics.

The author takes this opportunity of expressing his great indebtedness to Professor Millikan for initiating him into this work, and for much assistance and encouragement during its progress. He also wishes to heartily thank I. G. Barber, E. S. Akeley, I. S. Bowen, and Miss O. L. Risk for assistance with the observations.

RYERSON PHYSICAL LABORATORY,
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SEPTEMBER 22, 1922.

THE MOLECULAR SCATTERING OF LIGHT IN BENZENE, VAPOR AND LIQUID

By K. R. Ramanathan

Abstract

Scattering of sunlight by benzene, vapor and liquid, from 35° to 283° C.— The intensity of the light scattered at right angles was determined relative to that scattered by liquid ether at 35° C, by photometric comparison with the aid of reflecting prisms and a sectored disc. The relative intensity increased with the temperature at an accelerated rate; for the liquid, from 3.2 at 35° to 102 at 283° and, for the saturated vapor, from 0.95 at 182° to 11.9 at 267°. The scattered light is not completely polarized. The *imperfection of polarization* was measured by use of a double-image prism and a nicol. The ratio of the weaker to the stronger component, r, was found to decrease from 7.2 to 0.9 per cent for the vapor and from 43 to 2.8 per cent for the liquid as the temperature was raised from 35° to 280°. *Comparison with theories.* This imperfection has been attributed to the anisotropy of the molecules by Rayleigh, Born and others. The theory as extended by Raman to the general case of fluids leads to the relation $Sr/\rho(1 + r) = \text{const.}$, where S is the intensity and ρ the density. This is found to agree satisfactorily with the observations for both vapor and liquid. Since for the vapor, the intensity S increases with the temperature much more rapidly than the density, the Rayleigh law is not valid. The Einstein-Smoluchowski formula shows much better agreement, although, when calculated values of the refractive index and compressibility are inserted, it gives for the scattering in the vapor values which are 20 per cent or more too high.

Formula for isothermal compressibility of a saturated vapor is derived from Dietrici's equation of state. It is found to give the observed values for ether, isopentane and CO_2 in the temperature range 0.8 to 0.96 T_c if an arbitrary numerical factor 1.25 is used. Introducing this gives, for this range, $(dp/d\rho)_t = 2.5p(\rho_c - \rho)^2/(2\rho_c^2\rho - \rho^2\rho_c)$.

1. Introduction.

In his recent experiments on the molecular scattering of light in gases and vapors[1] Lord Rayleigh noticed the interesting fact that the light scattered in a direction perpendicular to the incident beam was not perfectly polarized. A similar effect has been observed but in a much more marked degree by W. H. Martin[2] in the light scattered by dust-free liquids. When we compare a liquid like ether and its vapor at the ordinary temperature in this respect, we find a large difference. Ether vapor at the ordinary temperature shows an imperfection of 1.7 per cent,

[1] Proc. Roy. Soc. A., Vol. 94, p. 453, 1918.

[2] Martin, Journal of Physical Chemistry, Vol. 24, 1920, p. 478, and Jan., 1922.

while liquid ether shows 8 per cent. The imperfection of polarization in gases has been explained [1, 2] on the assumption of anisotropy of the molecules; the imperfection in liquids is no doubt to be attributed to the same cause. The general theory of light-scattering in liquids has been discussed by Prof. C. V. Raman,[3] who has also put forward an explanation [4] of the increased imperfection of polarization of the scattered light in this case and suggested a quantitative connection between the intensity of the transversely scattered light, its state of polarization and the density of the fluid. A brief account of this theory is given in the course of the paper. The experiments described here were undertaken with a view to securing data regarding the intensity and polarization of the transversely scattered light both in the liquid phase and the saturated vapor phase of a suitable substance over a large range of temperatures. Benzene was chosen owing to the large value of its imperfection of polarization at ordinary temperatures. The result of the experiments has been to confirm the general validity of the explanation suggested.

2. Experimental Arrangements.

The apparatus used in the work is the same as that used by the author in an investigation on the intensity of the light scattered in ether.[5] The benzene was sealed in a stout-walled uniform glass bulb of about 1.2 inches internal diameter and the bulb was mounted in the center of an iron cross-tube (diameter 1.5 inches and each arm of the cross 15 inches long). The ends of the tube were closed with glass windows and it could be heated electrically by passing a current through a coil of nichrome wire wound uniformly over it. Temperatures could be maintained steady for long intervals of time to within half a degree. The benzene used was Merck's pure grade and was distilled five or six times in vacuo in the manner described by Martin.[6]

The intensity of the scattered light was determined by comparing the luminosity of a track of sunlight passing through it with a similar track in liquid ether kept in a rectangular glass bottle at the room temperature. The sunlight was focussed by two exactly similar lenses of the same focal length and provided with adjustable apertures at the center of the benzene bulb and at the center of the ether bottle. By means of two totally-reflecting prisms, the two tracks were brought

[1] Lord Rayleigh, Phil. Mag., Vol. 35, p. 373, 1918.
[2] Born, Deutsch. Phys. Gesell., Vol. 19, p. 243 (1917), and Vol. 20, p. 16 (1918).
[3] "Molecular Diffraction of Light," Calcutta University Press, 1922.
[4] Nature, July, 1922, page 11.
[5] Proc. Roy. Soc., Vol. 102, p. 151, 1922.
[6] Loc. cit.

side by side and their luminosities compared visually by means of a rotating sectored disc photometer.

The polarization of the light scattered at right angles to the incident beam was measured by means of a double-image prism and nicol. The double-image prism was mounted at the same height as the benzene bulb with its axis horizontal and pointing towards the bulb. It was first adjusted so that the two images of the horizontal track in the benzene were obtained in the same horizontal line and side by side with each other. The nicol was now inserted behind the double-image prism and so oriented that the vertical component was extinguished. On either side of this position, there is a position when the two images would be equal in intensity. If we denote the angle between these two equality-positions by 2θ, the ratio of the intensity of the horizontal component to that of the vertical is given by $\tan^2 \theta$.

3. Results.

The results regarding the scattering in the saturated vapor of benzene and in liquid benzene are collected in the following two tables.

Table I.

Scattering in Saturated Benzene Vapor.

S_t = Scattering at $t°$ C.
S_e = Scattering in liquid ether at 35° C.
ρ_t = density at $t°$ C.
r = Ratio of weak component to strong in the transversely scattered light.

Temperature $t°$.	$\frac{S_t}{S_e}$ Observed.	$\frac{S_t}{S_{182}}$.	$\frac{\rho_t}{\rho_{182}}$.	r (in per cent).	
				Observed.	Calculated.
35				7.2	
100				6.2	
182	0.95	1.00	1.00	3.5	3.2
204	1.56	1.64	1.48	3.4	2.8
228	3.00	3.15	2.25	2.5	2.2
247	4.9	5.14	3.00	2.0	2.0
267	11.9	12.5	4.5	1.5	1.2
280				0.9	

It will be seen that the intensity of scattering in both the saturated vapor and in the liquid increases rapidly with temperature becoming very large as we approach the critical temperature, and that in the case of the vapor, the increase is much more than in proportion to the density. The imperfection of polarization shows a diminution with increasing temperature tending to a very small value as we approach the critical point. In the last column of the two tables are shown the values of

imperfection of polarization calculated in the manner indicated in the next section.

TABLE II.

Scattering in Liquid Benzene.

Temperature $t°$C.	$\frac{S_t}{S_s}$.	r.	
		Observed.	Calculated.
35	3.2	43	44
125	3.67	32	31
182	5.48	19	16
205	7.21	14	10.3
228	11.0	9.5	7.0
268	20.5	3.0	2.9
280		2.8	
283	102		

4. POLARIZATION OF THE TRANSVERSELY SCATTERED LIGHT.

The theory of light-scattering by gases consisting of isotropic molecules as developed by the late Lord Rayleigh and the general theory of scattering of fluids as developed by Einstein on the lines of Smoluchowski's work, based on the idea of accidental deviation of density in the fluid, predict a perfect polarization of the light scattered in a direction at right angles to the incident beam. Einstein's expression for the fraction of the incident light scattered per unit solid angle in a transverse direction by unit volume of a homogeneous fluid is given by

$$\frac{\pi^2}{18}\frac{RT\beta}{N\lambda^4}(\mu^2-1)^2(\mu^2+2)^2, \qquad (1)$$

where T, β are the temperature and compressibility of the fluid, R is the gas-constant per gram-molecule, N the Avogadro-number, λ is the wave-length of the incident light and μ is the refractive index of the fluid. This reduces to Rayleigh's law in the case of gases obeying Boyle's law and experiments at Calcutta on a number of substances both in the liquid and vapor states have established the general validity of this law.

In the case of most media, however, the transversely scattered light is only imperfectly polarized. This imperfection has been attributed to the anisotropy of the molecules and the general case has been recently discussed by Raman. In such a medium, there is an extra scattering which is for the most part unpolarized, due to the anisotropy of the molecules. If Ω_0 denote the scattering arising from the fluctuations of density, $4\Omega_1$ the unpolarized scattering arising from molecular anisotropy and Ω_2 the polarized scattering due to the same cause, the ratio of the weak

component to the strong in the transversely scattered light is given by

$$r = \frac{2\Omega_1}{\Omega_0 + \Omega_2 + 2\Omega_1}. \tag{2}$$

In the case of a gas obeying Boyle's law, Ω_2 has the value $\frac{1}{3}\Omega_1$. The extra contribution from molecular anisotropy leads to an increased scattering in the ratio

$$\frac{6(1+r)}{6-7r}. \tag{3}$$

We shall assume this to be true generally.

If the molecules have absolutely random orientations, Ω_1 should be proportional to the number of molecules per unit volume. Since in the case of liquids and vapors, on rise of temperature, Ω_0 increases at a much larger rate than the density (in liquid the density actually decreases), the ratio $2\Omega_1/(\Omega_0 + \frac{1}{3}\Omega_1)$ should get smaller and smaller and reach a minimum value at the critical point where the value of Ω_0 is a maximum. We can easily deduce a quantitative relation between the intensity of the transversely scattered light and its imperfection of polarization. From equation (2), when $\Omega_2 = \frac{1}{3}\Omega_1$,

$$\Omega_0 = \frac{6-7r}{3r}\Omega_1,$$

and since $\Omega_1 = k\rho$, where ρ is the density of the substance,

$$\Omega_0 = \frac{6-7r}{3r}k\rho,$$

and the total scattering

$$S = \Omega_0 + \frac{13}{3}\Omega_1$$

$$= \frac{1+r}{r}\cdot 2k\rho;$$

$$\therefore \frac{S}{\rho}\frac{r}{1+r} = 2k, \textit{ a constant.} \tag{4}$$

In the last column of Tables I. and II. are given the values of r calculated from this relation. The constant k was calculated from the intensity and polarization of the transversely scattered light in saturated benzene vapor at room temperature. The imperfection of polarization was measured in an apparatus similar to that used by Lord Rayleigh, the vapor being illuminated by means of a strong beam of sunlight. The value of r was found to be 7.2 per cent as against Lord Rayleigh's value 6 per cent. The intensity at the room temperature was calculated, assuming the validity of the Rayleigh law of scattering (to which the

Einstein law reduces when the vapor is sufficiently rare) and applying the correction for the admixture with unpolarized light. The agreement between the calculated and observed values is satisfactory.

5. Calculation of the Intensity of the Transversely Scattered Light.

For calculating the intensity of the transversely scattered light according to the Einstein-Smoluchowski formula, the refractive index and the compressibility of the medium have to be known. The refractive index can be calculated, using Lorentz's relation $(\mu^2 - 1)/(\mu^2 + 2)\rho = 0.3423$ [1] for benzene (for the F line). There are no data for the compressibility of the liquid [2] or the vapor for the temperatures at which these experiments were made, but the compressibility of the vapor can be calculated from Dietrici's equation of state, viz.,

$$p = \frac{RT}{v - b} e^{-\frac{a}{RTv}} \tag{5}$$

with an empirical correction which can be determined in the manner described below. From (5)

$$\frac{1}{\beta} = -v\left(\frac{dp}{dv}\right)_t = p\left\{\frac{v}{v - b} - \frac{a}{RTv}\right\}.$$

Putting in the values of a and b in terms of the critical constants $b = v_c/2$ and $a/RT = 4b = 2v_c$ this reduces to

$$-v\left(\frac{dp}{dv}\right)_t = p\left\{\frac{2v}{2v - v_c} - \frac{2v_c}{v}\right\} = \frac{2p}{v}\frac{(v - v_c)^2}{(2v - c_c)}, \tag{6}$$

where v is the specific volume of the saturated vapor and v_c is the critical volume (volume of 1 gram of the substance at the critical point).

To test the applicability of this equation, the values of the compressibility of the saturated vapors of ether, isopentane and carbon dioxide were calculated and the values compared with the actual values obtained from the isothermal curves. The actual value of the compressibility is found to be larger than that given by equation (6), the ratio of the actual compressibility to that derived from (6) lying in the neighborhood of 1.25 over a large range. This ratio is plotted against the reduced temperatures. The points for the three different substances lie practically on the same curve, and from 0.8 T/T_c to 0.96 T/T_c the ratio lies near 1.25. In order to calculate the isothermal compressibility

[1] Landolt-Bornstein Tabellen, 1912, p. 1031.

[2] Except for the liquid up to 100°. For this case, the observed values of the scattering agree with the calculated.

of the saturated vapor of a substance for which the necessary isothermal pressure volume data are not available, we may multiply the compressibility given by equation (6) by the corresponding factor obtained from the curve. Calculating in this way, I find that the scattering in benzene vapor at 267° C. is 10 times that of liquid ether at 35°, while the observed value is 11.9 times. At other temperatures, the observed values are even higher than the calculated ones. This may be due either to the inapplicability of the above method of calculating the compressibility, or to the presence of a trace of impurity in the benzene which would give rise to an additional concentration scattering. The writer hopes to repeat the intensity measurements with carefully purified benzene.

This does not, however, in any way invalidate the main conclusion of the paper, namely, the proportionality of the unpolarized part of the scattered light to the density. The theoretical basis for this rests upon the assumption of the random character of the orientation of the molecules and the agreement of the experimental and theoretical values of the imperfection of polarization supports the assumption. This relation may not be true in the case of all liquids; with liquids whose molecules behave like electrical di-poles, the orientations are certainly not likely to be *at random*. Experiments on the polarization of the transversely scattered light with other liquids and over a large range of temperature are likely to furnish valuable information on the mutual influence of molecules in liquids.

In conclusion, I have much pleasure in recording my thanks to Prof. C. V. Raman under whose inspiring guidance the work described above was carried out in the laboratory of the Indian Association for the Cultivation of Science.

210 BOWBAZAAR STREET,
CALCUTTA,
August, 1922.

ADDENDUM.

A question has been raised as to the mean wave-length to be adopted in calculations when using composite light like sunlight for scattering experiments. In the above paper, the wave-length of the F line has been adopted. The influence of the wave-length of the incident light enters in two ways: (1) directly in the λ^{-4} factor and (2) indirectly through its influence on μ. When comparing two substances as regards their scattering, the effect of the first and dominant factor is identical in the two cases; that of the second depends on the dispersive powers of

the two substances. The values of $(\mu^2 - 1)^2(\mu^2 + 2)^2$ for liquid benzene and liquid ether at 20° C have been tabulated below:

Liquid Benzene at 20° C.

λ.	C 6,563 A.	D 5,893 A.	F 4,861 A.	G′ 4,340 A.
μ	1.4965	1.5011	1.5133	1.5236
$(\mu^2 - 1)^2(\mu^2 + 2)^2$	27.76	28.22	30.48	32.53

Liquid Ether at 20° C.

λ.	C 6,563 A.	D 5,893 A.	F 4,861 A.	G′ 4,340 A.
μ	1.3519	1.3538	1.3580	1.3607
$(\mu^2 - 1)^2(\mu^2 + 2)^2$	10.05	10.16	10.56	10.77

In benzene, the more dispersive substance, the difference between adopting the wave-length of the F line and that of the G′ line, for example, comes to nearly 6 per cent. At higher temperatures and for the vapor, the effect would be less and when we remember that our standard of comparison, ether, has itself a higher refractive index towards the violet, the difference between adopting the values of μ_F and $\mu_{G'}$ reduces to 4 per cent.

As regards the intensity of the scattered light in different parts of the spectrum, it will depend partly on the distribution of energy in the incident light and partly on the law of scattering. Adopting Abbot's values for the energy-distribution in sunlight, and assuming that the energy in the scattered light is proportional to λ^{-4}, the following are the relative values of the scattered energies:

λ in A.U.	Incident Energy I in Arbitrary Units.	$I\lambda^{-4}$.
6,000	5,050	3.9×10^{21}
5,400	5,700	6.7 "
5,200	5,900	8.1 "
5,000	6,080	9.7 "
4,800	6,250	11.8 "
4,400	5,820	15.5 "
4,000	4,350	17.0 "
3,800	3,750	18.0 "
3,500	2,700	18.0 "

The effect of the dispersion of the substance is to increase the relative importance of the radiations of shorter wave-length and more for a substance of larger than for one of smaller dispersion.

We have now to consider the visual effect of the scattered light. For ordinary luminosities, the maximum visual effect is produced by rays in the neighborhood of 5,500 A; but for the weak luminosities such as we here deal with, owing to the Purkinje effect, the region of maximum sensitiveness is shifted towards the blue, the shift being a function of the luminosity. Taking everything into account, the effective wave-length of the scattered light is probably a little farther on toward the violet than F; but considering the uncertainties in our knowledge of the luminosity-curves for weak illuminations and the smallness of the error when we use *scattered light for comparison*, the error introduced by adopting the wave-length of the F line for the calculations is not of a serious nature.

CALCUTTA,
November 28, 1922.

MINIMUM INTENSITY FOR AUDITION

By Frederick W. Kranz

Abstract

Minimum intensity of sound for audition for frequencies of 128 to 4,096 p.p.s.—(1) *Thermophone as source.* The receiver was held to the ear like a telephone receiver and was actuated by current from an oscillator, the threshold intensity being calculated from the corresponding current by Wente's formula. Tests of 14 ears for frequencies an octave apart show logarithmic sensitivities lying between the results of Wien and those of Fletcher and Wegel, the mean values increasing from 5 for 128 p.p.s. to a practically constant sensitivity of about 8.5 for the range 512 to 4,096 p.p.s. (2) *Telephone receiver as source* was then tried to see whether results nearer Wien's would be obtained. Two methods of calibration of diaphragm amplitude as a function of current were used, one involving the use of a microscope to magnify the motion of a quartz fiber attached to the diaphragm, the other amplifying the motion by means of a rocker which rotated a light mirror, both, however, involving extrapolation from relatively large amplitudes to those of the order of 10^{-9} cm. The results for two listeners agreed in showing a somewhat lower sensitivity with the telephone than with the thermophone as source, the energy ratio increasing from about 2 for higher frequencies to 7 for 128 p.p.s. This difference may be due to the extrapolation used in reducing the readings. The results of the two methods show a much better agreement with each other than with the results of Wien.

Suggested number scale for auditory sensitivity. Logarithmic sensitivity is defined as the $\log_{10}(1/J_0)$, where J_0 is the threshold intensity in ergs per cm^2 per second. The advantages of such a scale are pointed out.

In a previous paper by the author [1] a method was described by which determinations were made of the minimum sound intensity necessary for audition. The present paper is to give further results by this method and to present check measurements by a second method.

I. Thermophone as Source of Sound

The thermophone used consists of a thin strip of platinum foil about 0.0002 cm in thickness, mounted in a small telephone receiver case which was held tightly to the ear of the observer, thus forming a closed cavity containing the platinum strip and having the ear drum as one of the boundary walls. The alternating current flowing through the strip causes periodic variations in the temperature of the strip, thus heating the adjacent air, which periodically expands and produces pressure changes in the cavity. Thus there are no moving mechanical parts. The foil was also heated by a direct current of one ampere, the alternating

[1] Phys. Rev. 17, p. 384 (1921).

current and direct current being kept separate by condensers and inductance coils, the latter being about one henry each.

Because of the inefficiency of the thermophone, it was possible to measure directly the alternating current going into the thermophone by means of a thermo-couple and micro-ammeter, thus avoiding any uncertainties in reduction calculations. A resistance equal to that of the thermo-couple was placed in the line to keep the two sides of the electrical circuit balanced, and similarly the condensers and inductances were symmetrically placed as were the resistances used in the control of the current. The circuit arrangements are shown in Fig. 1.

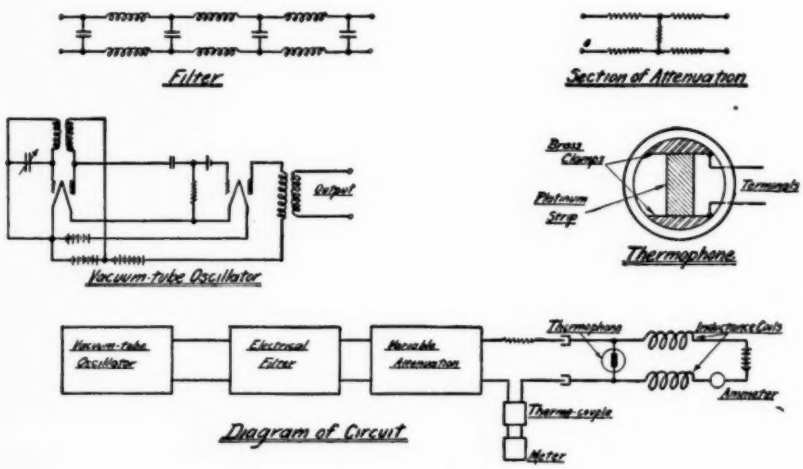

Fig. 1

The thermophone as used was held tightly against the ear so it can be regarded as producing pressure changes in a closed cavity, and the energy may be calculated from these pressure changes if the wave-length of the sound used is large compared to the dimensions of the enclosure. The formula for the amplitude of the pressure change in terms of the constants of the thermophone, as given by Wente,[1] was used. For the temperature and area of foil, volume of cavity, and the frequencies used in this experiment, this formula may be considerably simplified.

It becomes

$$\delta p = \frac{0.478 R I_0 i}{\sqrt{2}\,\frac{V_0 \alpha T_a}{2 p_0}\left(1 - \frac{k-1}{k}\frac{\theta_0}{T_a}\right)\left[(\gamma\omega)^2 + 8(\alpha\kappa)^2 + 4(\gamma\omega)(\alpha\kappa)\right]^{1/2}}$$

[1] Phys. Rev. 19, p. 336 (1922).

and substituting the constants of the air and the platinum,

$$\delta p = \frac{6.6 \times 10^5}{(273/\theta_0)^{3/4}(1 - .001\theta_0)} \left(\frac{RI_0}{V_0}\right) \left[1 + \frac{1.1}{\sqrt{f}} \left(\frac{273}{\theta_0}\right)^{1/4} + \frac{0.613}{f} \left(\frac{273}{\theta_0}\right)^{1/2}\right]^{-1/2} \left(\frac{i}{f^{3/2}}\right).$$

The quantities R, V_0, I_0, and θ_0 depend on the particular thermophone used and the amount of direct current used in it. The resistance R is the resistance of the foil when heated with the direct current I_0. In all of the measurements made, the value of I_0 was kept at one ampere. By means of a potentiometer arrangement in which the voltage drop across the thermophone was compared with that in another circuit, it was possible to determine the resistance of the foil with a current of a few milliamperes flowing through it in which case the heating is inappreciable, and also when the current was one ampere. This latter value was taken for R, while the difference between the two values allowed the temperature θ_0 of the foil to be calculated. The enclosed cavity V_0 includes the thermophone cavity and also the volume of the ear. The volume of the former was obtained from the dimensions while the ear volume was determined by placing the receiver cap of the thermophone tightly against the ear and filling the ear with water through the hole in the receiver cap. Thus the portion of the outer ear which actually contributed to the enclosed cavity as used was correctly taken into account. Substituting the values of R, V_0, I_0, and θ_0 gives δp as a function of f and i, the frequency and the alternating current.

In determining the limit of audibility, the thermophone was held tightly to the ear under test by means of a telephone head band, the other ear being covered by a dummy head receiver. The experiments were conducted in an isolated room, the walls and ceiling of which were lined with felt, so that disturbing external noises were eliminated. A second person opened and closed the alternating current circuit by means of a knife switch, and this current was reduced in small steps until the observer became uncertain in his judgments as to when the switch was opened and closed. The value of the alternating current at this point being read and the frequency being known, the corresponding pressure change in the cavity was determined by means of the formula given.

It is conceivable that the pressure change in the cavity might be diminished by the motion of the ear drum in response to the pressure on it. It can be shown that the pressure change without taking the movement of the drum into account should be multiplied by a factor which varies from unity to 0.75 as the elasticity of the ear drum is considered

to vary from ∞ to zero. It may be safely assumed, however, that the elasticity is sufficiently large to make the correction negligible, especially in view of the limits of accuracy of the determinations being made.

Although the determinations as made were of the values of the pressure changes exerted on the ear drum necessary for audition, calculations were made from these pressure changes of the intensities of the corresponding free progressive waves for the sake of comparison. If such a wave is reflected from a surface, the pressure changes exerted on the surface are twice the pressure changes in the wave. However the ear drum is at the end of a somewhat twisted canal, and the case is not that of simple reflection, and the above factor of two will be reduced. The irregularity of the canal does not allow an accurate calculation of the pressure on the drum, but considering the fact that it has approximately a uniform cross-section expanding but slightly just on reaching the drum and that its length is considerably shorter than the wave-length of the sound over the frequency range used, it seems that the intensities calculated from the observed pressure changes on the drum are not far from those of such free progressive waves as would be just audible.

The intensity J of a free progressive wave having a given value of pressure change may then be calculated from the formula $J = (\delta p)^2/2c\rho$, where c is the velocity of sound and ρ is the density of the air. In this case, the expression will be of the form $J = Ci^2/Lf^3$, where C is a constant depending on the thermophone and other factors mentioned, and L is the quantity given in brackets in the expression for δp. It may be noted that L is of the form $1 + A/\sqrt{f} + B/f$, where A and B are constants depending on θ_0 and, as used here, A is of the order of unity and B is of the order of 0.6, so that L is only slightly a function of the frequency f, varying by less than 10 per cent over the range of frequencies used. Thus the thermophone has an efficiency which is practically inversely proportional to the cube of the frequency and this serves to minimize the effect of harmonics in the alternating current supplied to the thermophone.

The results are given in terms of "logarithmic sensitivity," which is the logarithm to the base 10 of the reciprocal of the necessary intensity at the limit of audition, the intensity being expressed in absolute units, ergs per square centimeter per second. Thus the high parts of the curves represent the greater sensitivities and on the logarithmic scale equal differences in height have much more nearly equal importance in audition than if plotted on a linear scale, also small values are not obscured at the bottom of the paper. This logarithmic sensitivity seems to be the most logical way to express sensitivity. The numbers involved are small, equal differences between numbers are of approximately equal impor-

tance, the large ranges of sensitivity encountered in normal and deaf ears are easily expressed, and there is a very close connection with our absolute system of units as used in physical measurements. It is not necessary to give a name to the unit of sensitivity on this scale, as a "logarithmic sensitivity of 6" or even "a sensitivity of 6 units" has a clear meaning, once the system of calculation is understood.

The two ears even of the same individual have in general sufficient differences to be easily distinguished. Fig. 2 shows the results of tests

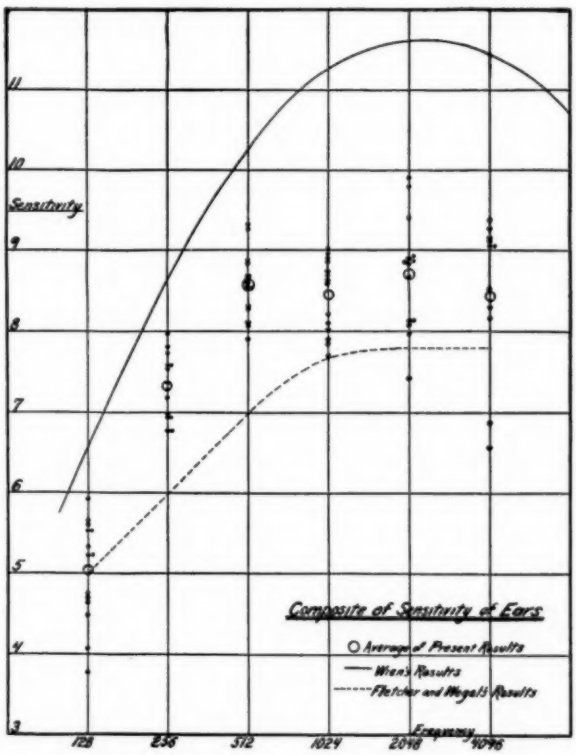

Fig. 2

made at intervals of an octave from 128 to 4,096 p.p.s. for 14 ears, and from this the variations between ears may be easily seen.[1] A sensitivity difference of 3 corresponds to an energy ratio of 1000, and variations of this magnitude are found between ears of people who would be classed as having normal hearing. The circles on this figure give the average

[1] The single figure of absolute sensitivity given in the author's previous paper does not agree with the highest values shown in the present data because of the use of the formula of Arnold and Crandall without the correction of the obvious error of a factor of θ_2, the absolute temperature. Wente's formula also includes another slight correction.

values of sensitivity for the ears shown. For the sake of comparison, Wien's [1] curve obtained by the use of telephone receivers is shown in the solid line. It is seen that the present results show a less sensitivity, that is a greater intensity required for audition, than found by Wien. The two sets of data agree in indicating a diminished sensitivity at the lower frequencies, but the present data show a less variation of sensitivity with frequency above 512 p.p.s. than indicated by Wien. The difference in sensitivity between the two sets of data varies from one and one half units to three units, the corresponding energy ratios varying from 30 to 1000. The dotted curve shows the averaged results of Fletcher and Wegel,[2] obtained fundamentally principally by the calibration of a telephone receiver by means of a thermophone. This curve falls below the average of the present results by a sensitivity difference of about one unit in general, except at the lowest frequencies, the two curves coinciding at 128 p.p.s.

II. Telephone Receiver as Source of Sound

Because of the difference between the results obtained by use of the thermophone and those obtained by Wien by use of a telephone receiver, it was considered advisable to make determinations of minimum audibility by means of a telephone receiver to parallel those of the thermophone as a check.

For absolute determinations with a telephone receiver, the amplitude of motion of the diaphragm must be found. At minimum audibility, the motion is so small that it cannot be measured directly. The method here used was to determine the relation between the diaphragm motion and the voltage across the receiver for larger amplitudes and extrapolate this relation downwards to small values.

Two methods of measurement of the amplitude of the diaphragm motion were used. In the first one, a light thin rod of wood about the size of a toothpick was waxed to the center of the diaphragm, the other end being split into a fork across which was fastened a fine quartz fiber. The telephone receiver was so mounted that the motion of the fiber could be viewed by means of a microscope having a micrometer eye-piece, and having such a magnification that one division of the scale in the eye-piece corresponded to a distance of 0.00087 cm. The telephone was thus calibrated for amplitude of motion of the center of the diaphragm per volt across the receiver for five frequencies from 128 to 1,536 p.p.s. The arrangement used in this calibration is shown in Fig. 3. The voltage across the receiver was calculated from the resistance and current in the

[1] Wien, Archiv fur die gesamte Physiologie **97**, pp. 1–57 (1903).

[2] Fletcher and Wegel, Phys. Rev. **19**, p. 553 (1922).

circuit across which the receiver is shunted. After calibration, the wooden stick with its fiber was removed from the diaphragm and an equivalent weight in the form of a small piece of brass was put on, so that the vibration characteristics would be maintained.

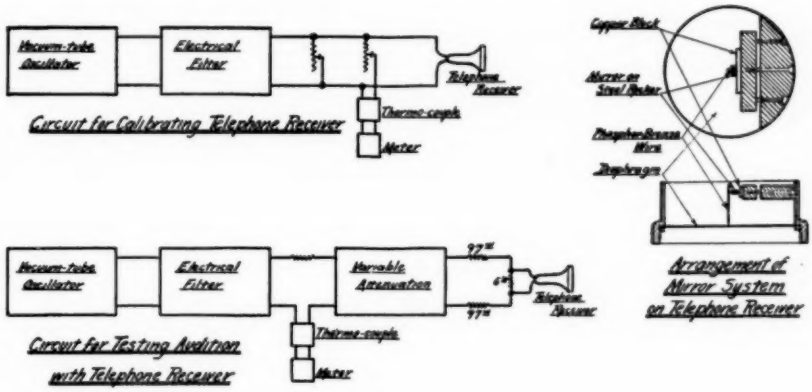

Fig. 3.

The circuit with which the receiver was used in determining the limit of audibility is also shown in Fig. 3. The attenuator is an arrangement of electrical resistances so adjusted that the different sections which can be introduced into the electrical circuit attenuate the current passing through by a definite known amount. A necessary condition is that the attenuator be terminated in a constant resistance, this being 200 ohms for this attenuator. As the impedance of the telephone receiver is neither pure resistance nor constant with frequency, a special resistance unit was made, consisting of a resistance of 6 ohms having connected to it on either side, resistances of 97 ohms. The telephone receiver was connected across the 6-ohm resistance, and since its impedance was large compared to the 6 ohms, the whole combination had a resistance of essentially 200 ohms, and this was connected to the output of the attenuator. The impedance offered by the attenuator to the circuit into which it is connected is 200 ohms regardless of the number of sections of the attenuator being used. The current into the attenuator was measured with a thermo-couple and a micro-ammeter, and the current output was easily calculable from the sections of attenuation thrown into circuit.

A unit of attenuation may probably best be defined in terms of the ratio of the electrical energy input to the electrical energy output, and for many purposes the relation between energy ratio and attenuation units may best be taken as a logarithmic one. So a unit of attenuation will be defined thus: $n = \log_{10} m$, where n is the number of attenuation

units corresponding to an energy ratio of m. Thus one attenuation unit corresponds to an energy ratio of 10, two units to a ratio of 100, four units to a ratio of 10,000, etc. The attenuator used has steps of 0.025, 0.05, 0.1, 0.2, 0.4, 0.8, 1.6, 3.2, and 6.4, a total of 12.775 attenuation units, and thus energy ratios could be obtained and accurately known from a change of 6 per cent to a ratio of about six trillion in steps of 6 per cent changes. Electrical energy being proportional to the square of the current, current reduction ratios may be easily calculated from the number of attenuation units used. Thus $n/2 = \log_{10} m'$, where n is the number of attenuation units corresponding to a current ratio of m'. The voltage across the receiver was calculated on the assumption that all of the current output of the attenuator goes through the 6 ohms which shunts the receiver. This assumption introduces an error of not over 6 per cent at low frequencies, decreasing to about 1 per cent at 1,000 p.p.s.

After calibration of the telephone receiver, measurements were made on the ears of two individuals and the necessary voltage across the receiver at the limit of audition was determined. The amplitude of motion of the telephone diaphragm was found from the calibration described above, and the pressure changes produced on the ear drum were then calculated from the relation $\delta p = p_0 \gamma \delta V / V_0$, where V_0 is the volume of the cavity formed by the diaphragm and case of the receiver and the ear, δV is the volume change produced by the motion of the diaphragm, and γ is the ratio of the specific heats of air.

The second method of measuring the amplitude of motion of the diaphragm was by means of a mirror so mounted as to rotate by movements of the diaphragm. In the first system of this type tried, a small mirror was fastened to a length of a hair spring from a watch and mounted in such a way that motions of the diaphragm acted on a projecting point on the back of the mirror, giving it a rotary motion. A line of light reflected from the mirror and on to a scale of ground glass was then broadened into a band of light corresponding to the amplitude of motion of the diaphragm. The objection to this system was that there was an uncertainty as to whether all of the motion imparted to the brass point by the diaphragm was taken up in producing rotation of the spring and mirror system or whether part of it was taken up in producing vibrations which of course would have no effect on the width of the reflected line of light and so would not be measured.

Because of this objection, another mirror system was used, for the suggestion of which the author's thanks are due to Dr. Max Mason. A sketch of this system is shown in Fig. 3. A phosphor bronze wire of

some stiffness was mounted to project from the center of the diaphragm and this rested against one sharp edge of a small rectangle of steel, another sharp edge being held against a copper block by the force exerted by a slight bending of the phosphor bronze wire. This force was regulated by adjustments of the position of the copper block which was fastened to the receiver case. Thus movements of the diaphragm caused the wire to rock the steel piece about the edge which rested on the copper as an axis. A small mirror waxed on to the steel piece gave a broadening of a reflected line of light just as in the other mirror system. The steel piece was about 1 × 1.5 mm in size. The great advantage of this system is that it has no natural period of its own since it has no elastic force separate from the diaphragm. The mirror and steel piece merely add a little mass to the moving system, and should follow the motions of the diaphragm faithfully. The sharpened edges of the steel piece make grooves in the wire and in the copper block, and rock in these.

The relation between diaphragm motion and the width of the band of light was found by use of a micrometer screw. The telephone receiver used was so made that the portion back of the diaphragm, including the pole-pieces, could be removed without disturbing the clamping of the diaphragm, so the micrometer screw was mounted on a frame with the clamped diaphragm, and the center of the diaphragm was deflected by pushing it with the end of the micrometer screw and the resulting movement of the line of light reflected from the mirror was noted. An amplification of 1,600 was obtained, that is the motion of the line of light as indicated by its broadening was 1,600 times the amplitude of the diaphragm motion, the amplitude of motion of the telephone diaphragm being determined in terms of the voltage across the receiver. With this system, measurements were made on the sensitivity of the ear with the receiver in the same condition as when calibrated, the mirror attachment remaining in place. Tests were made at five frequencies between 128 and 1,536 p.p.s.

A determination of sensitivity was made by the thermophone method in each case just before making a measurement with the telephone receiver, thus giving quite a direct comparison of the results by the two methods. The results are tabulated below, S and K refer to two different observers and R and L to the right and left ears. The first method is that in which the diaphragm amplitudes were measured by means of a microscope, and the second that in which the vibrating mirror was used.

METHOD 1

Frequency	Ear		Sensitivity		Difference in Sensitivity (1)−(2)	Energy Ratio
			Thermophone (1)	Telephone (2)		
128.....	S	R	5.44	5.12	0.32	2.1
		L	5.57	4.62	0.95	8.9
	K	R	4.96	4.33	0.63	4.2
		L	5.18	4.53	0.65	4.5
256.....	S	R	7.63	7.01	0.62	4.2
		L	7.86	6.72	1.14	14
	K	R	7.47	6.41	1.06	11.5
		L	7.37	6.51	0.86	7.2
512.....	S	R	7.87	7.59	0.28	1.9
		L	8.69	8.39	0.30	2.0
	K	R	8.62	8.09	0.53	3.4
		L	8.32	8.39	−0.07	0.83
768.....	S	R	7.65	7.71	−0.06	0.87
		L	7.63	7.61	0.02	1.05
	K	R	9.33	9.05	0.28	1.9
		L	9.43	9.15	0.28	1.9
1,536	S	R	8.78	8.95	−0.17	0.67
		L	7.86	7.95	−0.09	0.83
	K	R	8.78	8.71	0.07	1.2
		L	8.78	8.41	0.37	2.4

METHOD 2

Frequency	Ear (K)	Sensitivity		Difference in Sensitivity	Energy Ratio
		Thermophone	Telephone		
128.....	R	5.45	4.34	1.11	13
	L	5.28	4.34	0.94	8.8
256.....	R	7.53	6.89	0.64	4.4
	L	7.32	6.61	0.71	5.2
512.....	R	8.58	8.3	0.28	1.9
	L	8.48	8.1	0.38	2.4
640.....	R	9.24	8.60	0.64	4.4
	L	9.24	8.64	0.60	4.0
1,024.....	R	9.21	8.94	0.27	1.86
	L	8.82	8.44	0.38	2.4
1,536.....	R	8.84	8.74	0.10	1.26
	L	8.35	8.24	0.11	1.28

It is seen that the sensitivities obtained with the thermophone are in general somewhat greater than those obtained with the telephone; that is, the necessary energy for audition is less as measured by means of the thermophone than as measured by means of the telephone. The two telephone methods agree well in this. The ratio of the two measured values of this energy is given in the last column. The averaged values of these energy ratios follow.

Frequency:	128	256	512	640	768	1,024	1,536
Energy ratio:	6.9	7.7	2.1	4.2	1.4	2.2	1.3

The uncertainty in determining the limit of audition is greater at the lower frequencies than at the higher, but mere uncertainty should not make the ratios all larger, as is found to be the case.

It is seen that the telephone measurements agree with those obtained with the thermophone in giving considerably lower values of sensitivity than found by Wien.

Discussion

As to the difference found between thermophone and telephone results, in the latter measurements, the relation between diaphragm amplitude and voltage across the telephone receiver was determined for amplitudes down to about 6×10^{-4} cm, and this relation was used at the limit of audibility where the amplitude of the diaphragm motion varied from about 10^{-7} cm for the lowest frequency to 10^{-9} cm for the higher frequencies. In the range where observations were possible, this relation was found to vary somewhat with the amplitude, the variation being such that the amplitude per unit volt was greater for the larger amplitudes than for the smaller. This variation was not large but was found consistently with both methods of measurement of the diaphragm amplitude, so it may be possible that the extrapolation to the small amplitudes should not be made linearly. This variation is in the right direction to explain the difference in results between the telephone and the thermophone, for if the telephone became less and less efficient at lower amplitudes, it would take a larger amount of electrical energy to produce a given motion of the diaphragm than a linear extrapolation would indicate, and this corresponds to a decreased sensitivity of the ear as measured with the telephone, which is what is found if the thermophone be taken as a standard. Also it may be that the statistical theory of condensations and rarefactions in the propagation of sound impulses may not hold accurately when the amplitudes of motion are as small as are here considered, these being, for the higher frequencies, of the order of one thirtieth of the diameter of a nitrogen molecule and about one ten-thousandth of the mean free path of the molecules.

The agreement between the values for the necessary energy at minimum audibility obtained by the use of the thermophone and the telephone is sufficiently close, however, to leave no uncertainty about the order of magnitude of the sensitivity of the human ear.

It is recognized that tests of minimum audibility at a rather few separated frequencies do not justify any conclusions being drawn as to the form of the curve of audition in the intervals between these frequencies. A method has been developed which eliminates this uncertainty and allows a complete curve of audition to be made. Many such curves have been obtained and will be published soon.

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